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ISOTHERMAL VAPOUR LIQUID EQUILIBRIA FROM
ISOBARIC DATA

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

by

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to the

DEPARTMENT OF CHEMICAL ENGINEERING
Indian Institute of Technology, Kanpur

February 1972



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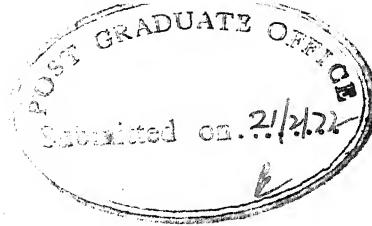
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CERTIFICATE

It is certified that this work has been carried out under my supervision and that has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENTS

The author expresses his gratitude to Dr. Mamata Dutta for her guidance, encouragement and valuable discussions.

The author acknowledges with thanks the ready help provided by the staff of the Glass Shop and Chemical Engineering Workshop.

The help of Mr. D.S. Panesar in careful preparation of drawings and Mr. B.S. Pandey for meticulous typing of the manuscript is highly appreciated.

Finally the author is indebted to the Council of Scientific and Industrial Research, Government of India for the grant of a Junior Research Fellowship to support the work.

Author

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ABSTRACT

The isobaric vapour-liquid equilibrium data have been measured for the system Methylcyclohexanol + Methylcyclohexane. The equilibrium still, as designed by Yerazunis, Plowright and Smola has been used for this purpose after some modifications. The data have been tested for thermodynamic consistency using the integral test. Also, a method for the prediction of isothermal vapour-liquid equilibrium data from isobaric vapour liquid equilibrium data has been developed. It is based on the introduction of temperature dependence of the constants in Redlich-Kister equation for excess Gibb's energy. It has been found satisfactory for simple as well as complex mixtures.

CHAPTER 1

INTRODUCTION

Experimental vapour liquid equilibrium studies still continue both for the purpose of collecting data useful for design of industrial distillation units and for a theoretical understanding of the behaviour of liquid mixtures.

The present investigation deals with the vapour liquid equilibria of hydrocarbon + alcohol mixtures. According to the work done so far it is generally found that the azeotropes are formed in such mixtures when there is a large difference in molecular size and structure of the two components. Examples are Methanol + Toluene¹⁶ (azeotrope at .88 mole % MeOH), Ethanol-Benzene¹⁷ (azeotrope at 50 mole %), Propanol-Benzene¹⁸ (azeotrope at 35 mole % PrOH), Propanol-Cyclohexane¹⁹ (azeotrope at 60 mole % PrOH), Propanol-Hexane²⁰ (azeotrope at 5 mole % PrOH) etc. However, if one wishes to isolate the effect of H - OH interactions on the vapour liquid equilibrium data one should study mixtures of components having same level of molecular size and structure. Studies carried out in this direction in the literature are for systems Toluene + Phenol,²¹ Methylcyclohexane + Phenol,²¹ Benzene + Cresol.²² Recently Mukherjee²³ studied the following systems Methylcyclohexane, Heptane and Heptanol-Toluene. These do not show any azeotropic behaviour. This work is essentially a continuation in this direction. The system chosen is Methylcyclohexanol+Methylcyclohexane. From the behaviour of the above systems it is expected

that the system Methylcyclohexanol + Methylcyclohexane will not show azeotropic behaviour.

Isobaric vapour liquid equilibrium data have been measured for the above mentioned system. The equilibrium still used for such determination is the one designed recently by Yerazunis,⁵ Plowright and Smola. This works on circulation of both vapour and liquid phases. The highlights and special features of this still are given in the second chapter.

Isobaric vapour liquid equilibria does not directly give a clear picture of non-ideality and behaviour of excess Gibbs energy of mixing. The information is rather diffused. However, a method has been developed to predict isothermal data from isobaric data and is based on the introduction of temperature dependence of the constants in the Redlich-Kister equation for excess Gibbs energy. The predictions agree well with experimental data for a number of systems, and in this process it is revealed that isobaric data if handled carefully can give lot of information regarding the behaviour of non-ideal solutions.

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CHAPTER 2

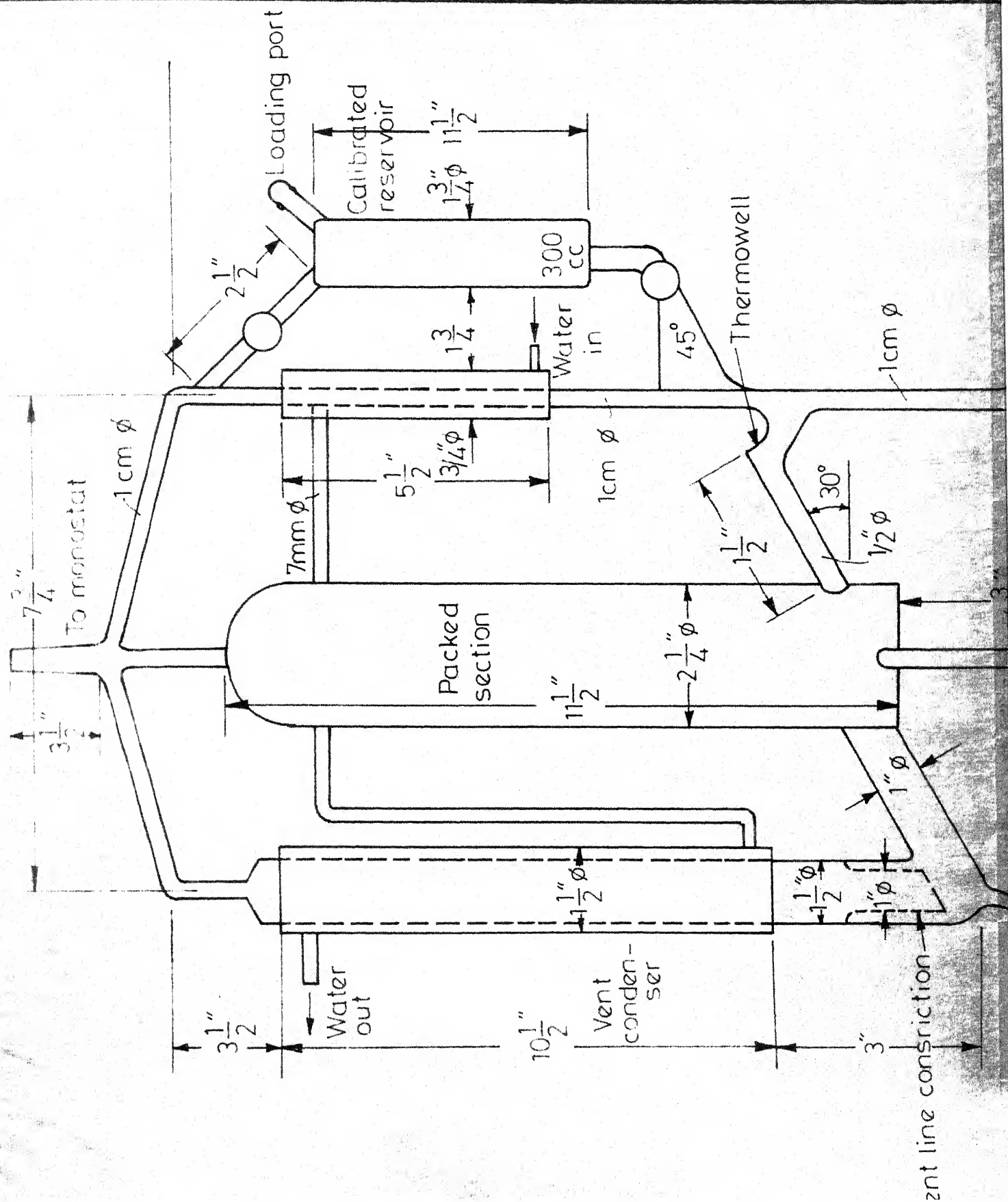
EXPERIMENTAL SET-UP AND PROCEDURE

The need for accurate vapour liquid equilibrium data has given rise to a large number of equilibrium stills - the apparatus in which vapour pressure, temperature and composition are usually measured. Before describing the equilibrium still used in the present study a brief history of the development of the equilibrium stills will not be found out of place. It was Othmer¹ who successfully operated a still of the vapour recirculatory kind. Other workers made several other modifications. However, heat losses leading to partial condensation, inadequate mixing of the recycled vapour condensate with the liquid in the reboiler still remained the major drawbacks. Jones et.al.² devised another still of the vapour recirculation type in which heat losses in the vapour tube were compensated by external heating, mixing in the boiler was promoted by bubbling the returning vapour through a nozzle in the reboiler. High internal pressure drop, inexact measurement of equilibrium temperature, and the need for exact compensation of heat losses (undercompensation led to stoppage of circulation and over compensation led to overloading of the vaporizing tube with the liquid) checked any further attempts at modification of the still in this direction. Gillespie³ designed a still which overcame many of the defects discussed above. It was based on the vapour-recirculatory principle but differed from other types in that the boiling liquid is also circulated rapidly by employing

the Cottrell device⁴. Landwehr, et.al. modified Gillespie apparatus - by separating the point of liquid sampling from the reboiler, lagging the vapour in the separation chamber by recycle liquid stream. The present still is a highly improved version of the Gillespie still, overcomes certain basic flaws in the Landwehr design also. This has been developed at Rensselaer Polytechnic Institute by Yerazunis, et.al.

The Equilibrium Still (Fig.1):

This remains basically a vapour and liquid recirculation device. Its most distinguishing feature is to be found in the details of the separation chamber (Fig.2). The liquid and vapour are not permitted to separate within the boiler, but are maintained in intimate contact as they rise up the Cottrell pump in the form of slugs to the separation chamber. Vapour and liquid mixture at the top of the Cottrell pump is directed downward by a reverse bend through a short column packed with glass beads. The mixture gets separated only after it has passed through the packed section. The liquid streams past a thermocouple in the thermowell and overflows to the receiver-mixer bypassing the liquid sampling cell. The vapor flows upward around the packed column and thence downward around the entire separation chamber providing a thermal barrier to the separation region. The vapour stream then passes into a condenser, the condensate from which flows to the receiver-mixer bypassing the vapour condensate sampling cell. The stream of hot liquid disengaged from the vapor within the separation chamber is combined with the recycling condensate



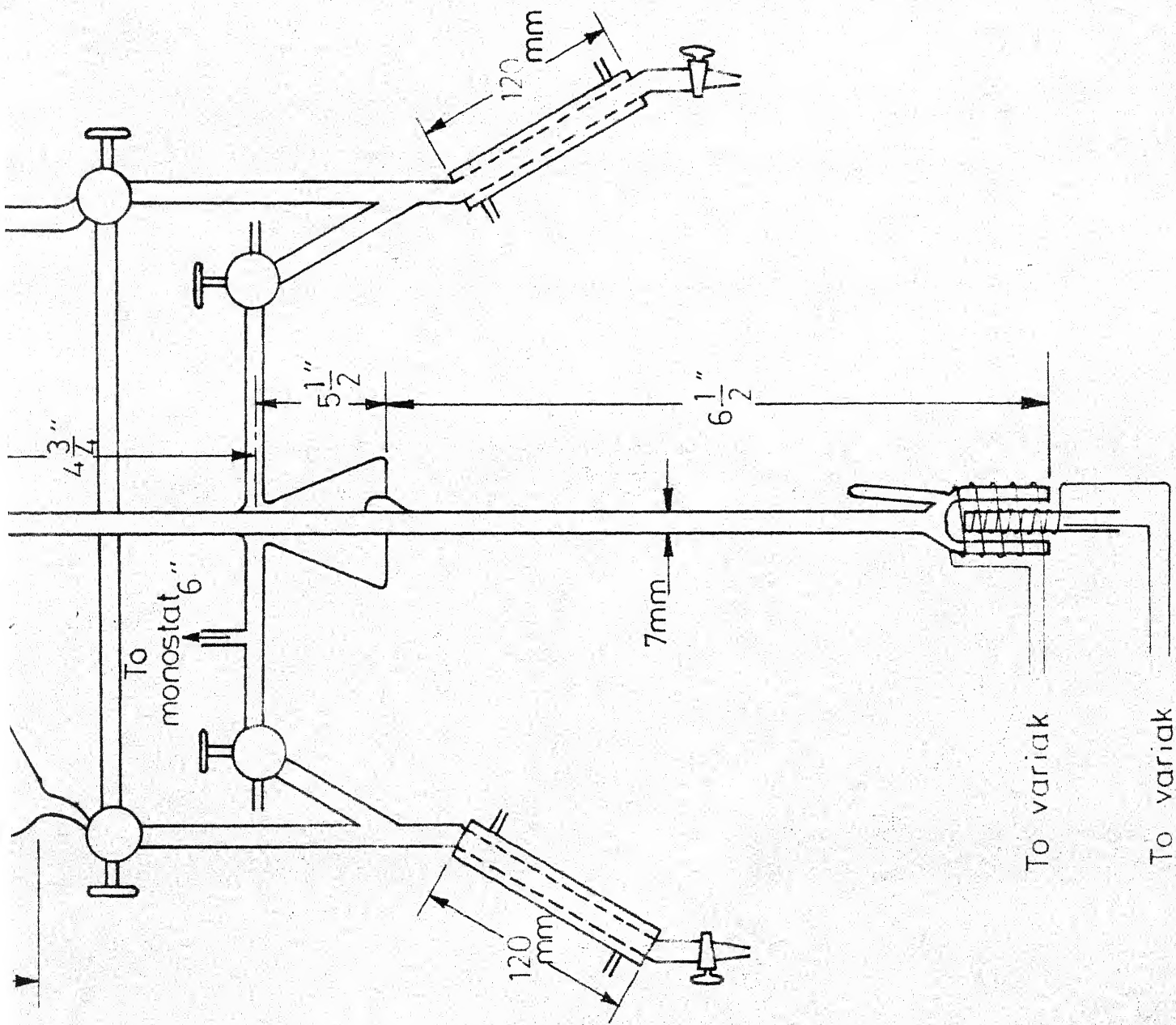


Fig.1 - Equilibrium still.

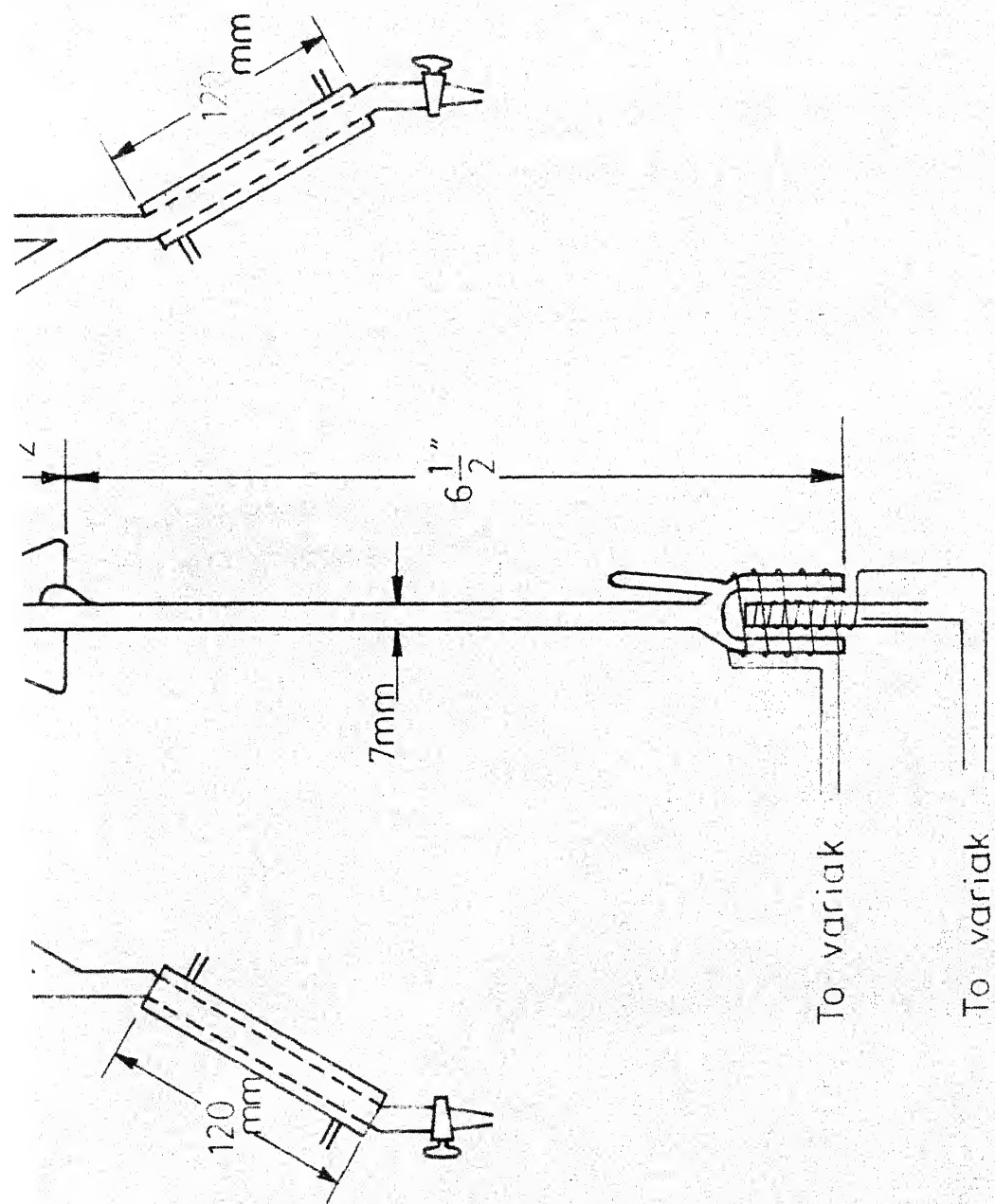


Fig.1 - Equilibrium still.

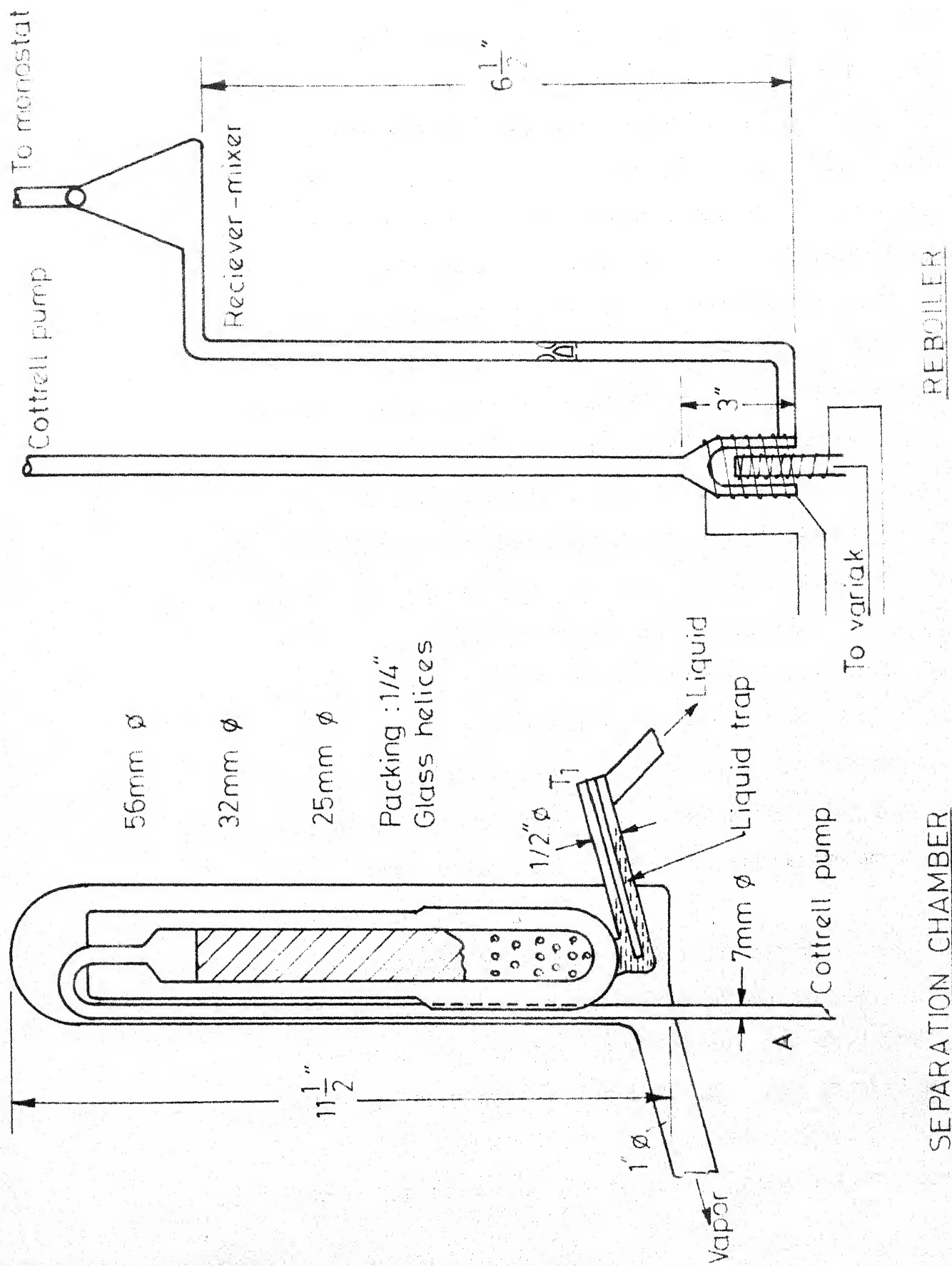


Fig. 2.

before it returns to the boiler in the receiver-mixer. The mixing is enhanced by increasing the interfacial area by putting glass beads in the mixer. The use of a magnetic stirrer has been avoided in this way. The main features of this still are:

- (i) equilibrium temperature is measured, after ensuring equilibrium between the boiling liquid mixture and its vapour at the point where the two disengage in the separation chamber and not in the reboiler. This avoids measurement of temperature of superheated liquid and ensures measurement of the correct equilibrium temperature.
- (ii) packed column in the separation chamber provides additional (in addition to the Cottrell pump) contact for the two phases to approach equilibrium. Because the vapour and liquid in the Cottrell pump exist in the form of slugs the equilibrium is attained there only on a local basis. The packed column, by providing additional interfacial area, serves to smear out the local fluctuations and raises the equilibrium to an integral basis
- (iii) partial condensation and reflux of the vapour in the separation chamber is prevented by using the vapour phase as a thermal barrier. Landwehr has used the liquid recycle stream for lagging. But if we look at it more closely there is a positive gain in using vapour for lagging. In vapour lagging latent heat of

condensation is involved and in liquid lagging the sensible heat is involved. Since latent heat is much more than the sensible heat, vapour lagging is more advantageous.

- (iv) sampling of liquid and vapour condensate is possible without stopping recirculation and without disturbing the equilibrium. The vapor sampling cell is not of the conventional overflow design and therefore there is no enrichment of the more volatile component which may occur between termination of recirculation and sample removal.
- (v) Entrainment of vapor with liquid recycle in the separation chamber has been avoided by the creation of a liquid seal around the thermowell.
- (vi) the use of the receiver-mixer eliminates the existence of any concentration gradients in the reboiler. It is clear that at equilibrium the liquid-vapor mixture leaving the boiler is identical in quantity and composition with the combined liquid streams returning to it.
- (vii) all portions of the equilibrium still - vapour-side condenser, liquid-side condenser, reservoir, sample cells, receiver-mixer are separately connected to the manifold. This ensures a uniform pressure throughout and eliminates the chances of internal pressure drop.

- (viii) for prevention of heat loss to the surroundings the separation chamber has been surrounded by a double-walled, silvered and evacuated jacket.

This still differs in few aspects from the one designed by Yerazunis et.al. Firstly the vapour and liquid sampling loops have been altered. Whereas previously each loop had three three-way stop cocks. We have used only two 3-way stop cocks on each side, and the sample cells are connected to the manifold so that they are under system pressure. When the equilibrium still is in operation so that the withdrawal of sample into the sample cells is done at the equilibrium pressure. Second alteration is in that the connection of the equilibrium still to the manifold is done through a third additional water condenser. This prevents any escape of vapour into the manifold. Lastly, the drainage port in the reboiler has been eliminated by completely sealing off the reboiler. For purpose of drainage the seal is cut and liquid removed by means of a syringe. This change had to be made because the compounds under study (viz. methylcyclohexanol and methylcyclohexane) were eating away the grease.

General Arrangement of the Apparatus:(Fig.3)

The manifold consists of a 6 ft., 1" diameter copper tube with six connections. Two connections on the left with an opening of 1/4" diameter are connected through a pair of toggle valves - one to the nitrogen cylinder and the other to the vacuum pump. The third connection is via a brazed tee joint to the surge tank.

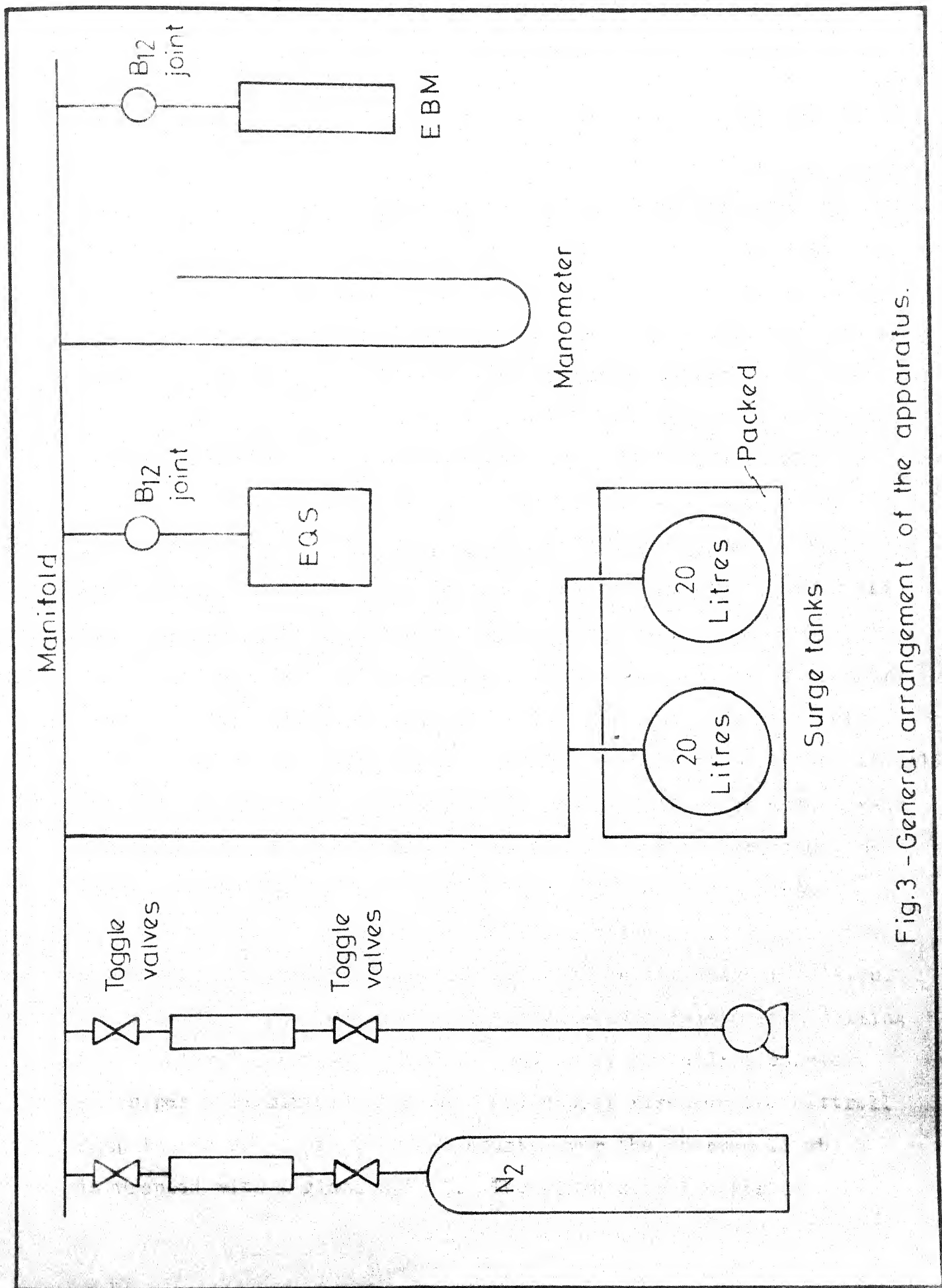


Fig.3 - General arrangement of the apparatus.

The surge tank consists of two 20 liter round bottom flasks. The other three connections are one each to the equilibrium still, manometer and ebulliometer. Equilibrium still and ebulliometer connections employ ground glass B-12 joints so that at any time they can be isolated from the manifold. Vacuum tubing is used to make the copper-glass connections. Manometer is directly connected to the copper line through a vacuum tubing.

The two 20 liter round bottomed flasks which function as the surge tanks are kept in a wooden box packed with insulating material - which lends a thermal stability to the surge tank. This large volume acts as a damper to pressure fluctuations that may arise in the system due to changes in room temperature, irregular heat losses, voltage fluctuations, sampling etc.

Manometer has been used for rough measurements of pressure. Accurate measurement of pressure is done by means of the single stage ebulliometer (Figure 4). The ebulliometer permits exceptionally precise measurements of boiling temperature. If we know the exact dependence of boiling point on pressure for a pure substance, by measuring the boiling points of this substance we can measure pressure over any range. Water, benzene, toluene are some of the substances for which P-T dependence is known with high precision.

The ebulliometer (Fig.4) essentially consists of a boiling tube, cottrell pump, thermowell, condenser, and a drop counter. The super heated mixture of liquid and vapour rises up the cottrell pump in the forms of slugs and spurts over the thermowell which is wrapped with a glass spiral. The glass spiral helps in

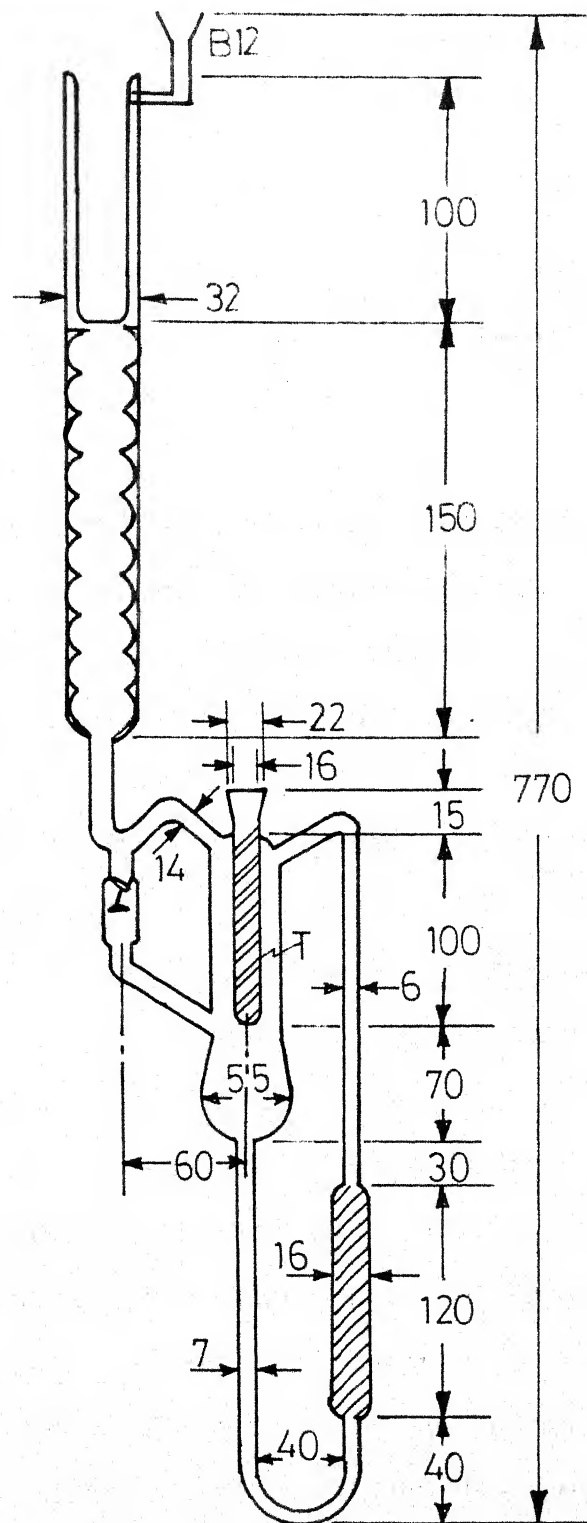


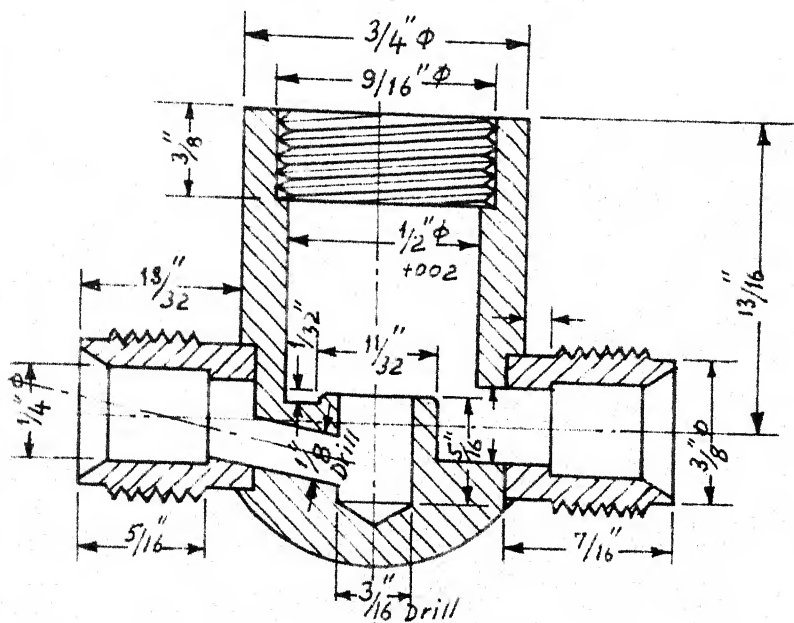
Fig. 4 -One stage Ebulliometer.

breaking the liquid-vapour mixture. The liquid at this point loses some of its superheat and the equilibrium temperature is measured from the thermowell. The vapour rises up the condenser, condenses and recycles into the boiling tube by trickling in the form of drops from the drop counter. The drop rate is a measure of the intensity of heating. Operation is done over a range of drop rate, in this range the boiling point essentially remains constant. The lower limit signifies inadequate heating and the higher limit signifies excessive heating. A float trap has been provided in the recycle path so that the boiling liquid should not rise up on the other side also.

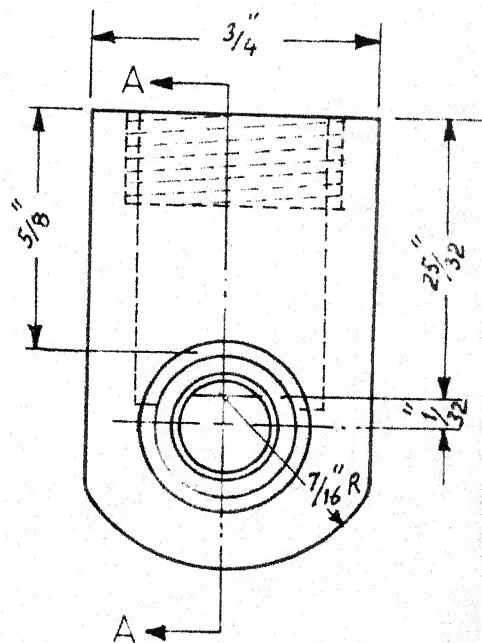
Toggle valves are snap action valves, their opening time being few seconds. These valves have been used in conjunction, with small volume metal accumulators, they facilitate change in the system pressure by as small a magnitude as $\pm .5$ mm Hg. (Fig.5)

Heat supply to the reboiler is done by means of two heaters - one external and the other finger heater. The finger heater consists of a ceramic rod over which the Nichrome wire of gage 22 is wound. It has a total resistance of 19 ohms. The external heater is wound helically by the same nichrome wire. This provides a resistance of 25Ω . Heating of the boiling tube of the ebulliometer is also done by nichrome 22 gage wire (20Ω) wrapped helically over it. All the three heaters are connected to the main supply through variable transformers.

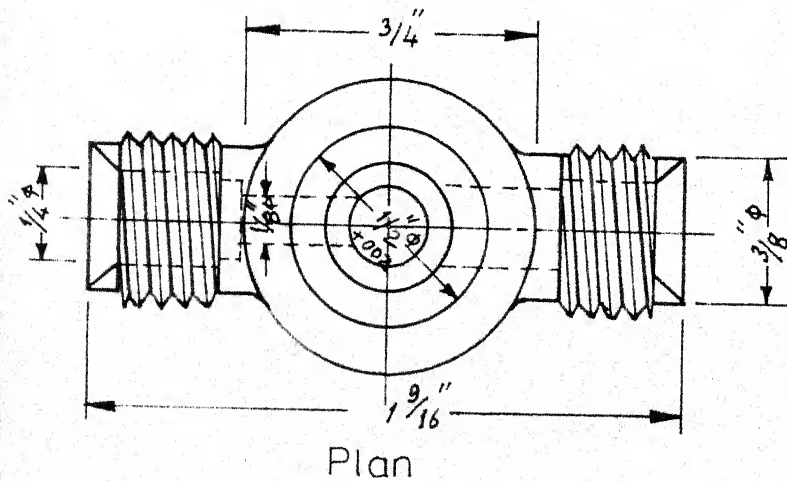
Tap water has been used for condensation. The vapour,



Section A:A



Side View



Plan

TOGGLE VALVE (BODY)

Fig. 5.

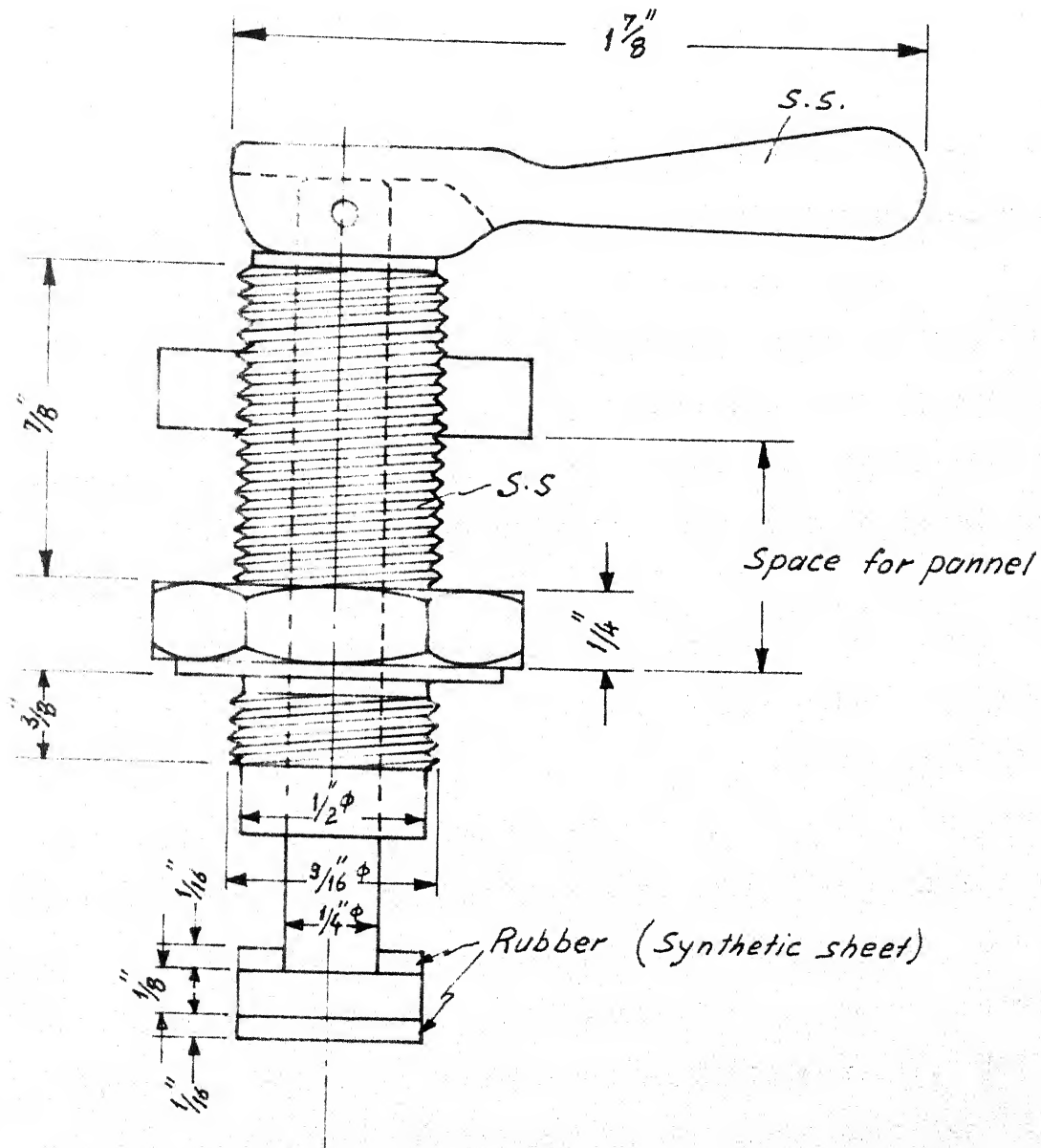


Fig.5a-Toggle Valve Stem.

condenser, liquid side condenser and the additional condenser are connected in series. The sampling cell coolers form another set connected in series.

Experimental Procedure:

Before the collection of data for the binary system involved (methylcyclohexanol - methylcyclohexane) the whole set-up was standardized so that one could be certain about the attainment of equilibrium and affect change in the equilibrium point (say from x' , y' , T' to x'' , y'' , T'') by easy control of operating conditions (pressure, voltage or heat input, vapor and liquid recirculation rates etc.). Details of standardization have been included in the Appendix.

Prior to the charging of liquid into the reboiler the whole system (surge tank, manifold, equilibrium still) was purged of air by means of a vacuum pump. When the manometer reading was essentially zero, suction was stopped. Inert gas nitrogen was then fed in through the toggle valves so that system pressure was 760 mm. Hg. Ebulliometer filled with 60 cc of Analar Benzene was plugged to the manifold. The calibrated reservoir in the equilibrium still was filled with 200 cc of purified methylcyclohexanol. The loading port was closed and the two two-way stop cocks connecting the reservoir to the system were opened. This brought the reservoir to system pressure. The liquid trickles down to the reboiler along the path of liquid recycle stream, creating a temporary hold up in the receiver mixer. When all of the liquid has reached the receiver-mixer the reservoir is isolated from the system. To shorten the time of total

transfer of the liquid to the reboiler, the heaters (external and finger heater both) are put on, the temperature gradient so created helps in quick and rapid flow to the reboiler. Simultaneous to the putting on of reboiler heaters, the ebulliometric heater is also put on, and the flow of water through all the condensers (liquid-side, vapour-side, sampling cells, ebulliometric condenser) started.

Attempt is now made to achieve the equilibrium steady state. As revealed by standardization procedure the equilibrium is reached under steady condition of pressure, when (i) there is rapid movement of slugs of liquid and vapour over the entire length of cottrell pump, (ii) liquid seal is formed around the thermowell- so that there is no entrainment of vapours with the liquid recycle stream, (iii) there is no hold-up in the receiver-mixer, (iv) vapour recirculation rate is high. Visual observation is made to confirm these facts. Voltage is adjusted to control these factors.

For pressure adjustment recourse of N_2 and vacuum pump is taken. Initially one finds that the pressure in the system increases. This is due to expansion of N_2 at the higher temperature. Manometer registers an increase of as much as 10 to 15 mm. If the system pressure exceeds 760 mm. which it does normally, pressure is reduced by vacuum through the toggle valves. They are opened and closed alternately. The pair of toggle valves working in conjunction with the small accumulator are suitable to affect a change of ± 0.5 mm.Hg. The large volume provided by the surge tank also aids in this precise control. Pressure is read from the ebulliometer. At 760 mm.Hg

the ebulliometer should exactly reproduce the normal boiling point of benzene, that is 80.10°C .

When steady state regarding the system pressure has been reached one looks for the equilibrium steady state. The temperature read from the thermocouple in the separation chamber thermowell, should stop fluctuating. When the potentiometer indicates a constant value of emf for about 15 min. - the steady state is believed to have been reached. System pressure is again checked from the ebulliometer reading. Temperatures - equilibrium and ebulliometric are measured by a copper-constantan thermocouple which has been previously calibrated against a platinum resistance thermometer.

Vapour and liquid samples are now withdrawn simultaneously into the sample cells. Because three-way stop-corks are used recirculation is not interrupted. The samples are allowed to cool for about five minutes. The cells are disconnected from the system by closing their connection to the manifold, and vented to the atmosphere. The vent prevents any contamination of the sample with extraneous material from outside during the time of removal. The samples are collected in sample tubes - the amount being approximately 1 cc. The samples are analysed on a refractometer which has been previously calibrated. The refractive indices measurement provides an accuracy of approximately .5% to the vapour and liquid compositions.

The same steady state is double checked by taking a second set of readings - x , y and T . Time interval kept between the two readings varied between 45 min. to 1 hour.

To effect a shift in composition, after the above determination was made, a few milliliters (15 cc to 20 cc) of the liquid were drained through the sampling line, and roughly the same amount of the second component was added through the loading port. This procedure of changing the composition was continued till it was no longer economical i.e. the addition of the second component brought little or no change in the equilibrium temperature. The reboiler, at this point, was emptied the system cleaned and the other pure component was filled in. Thus the data was collected in two parts - one starting from pure methylcyclohexanol and two starting from pure methylcyclohexane.

About 18 data points were obtained for the entire range. In addition the boiling points of the pure components were also determined and the pure liquid and pure vapour samples for both the components were also analyzed on the refractometer to confirm the purity of the samples.

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CHAPTER 3

SOURCE AND PURITY

Methylcyclohexanol was obtained as laboratory grade from Riedel and Methylcyclohexane was supplied as Analar grade from Fluka. Methylcyclohexanol was purified by a process of successive distillations and the purity after each distillation was checked on a differential ebulliometer - this ebulliometric determination (Figure 6) of purity has been extensively used by Sweitslawski.¹⁵ The differential ebulliometer measures the boiling point and the condensation temperature of the liquid in question when equilibrium conditions have been reached. The difference (ΔT) between the two temperatures indicates the extent of purity - the smaller the difference purer is the compound or it has lesser impurities.

The distillation of methylcyclohexanol was performed in a column (5 ft. column length and Internal Diameter = 40 mm) packed with glass helices (average length = 12 mm and O.D. = 5 mm), under vacuum and in an inert atmosphere of Nitrogen. The distillation head was designed for reflux - under normal conditions it gives a reflux ratio of 1:1. However to improve the reflux ratio the distillate was collected intermittently - for 10 minutes it was on reflux and then for the next 10 minutes it was kept on total reflux. Details of the distillation process are being given below:

Pressure of the system. = 100 mm - 120 mm Hg. absolute

Temperature of the = 95 to 100°C
condensing vapours

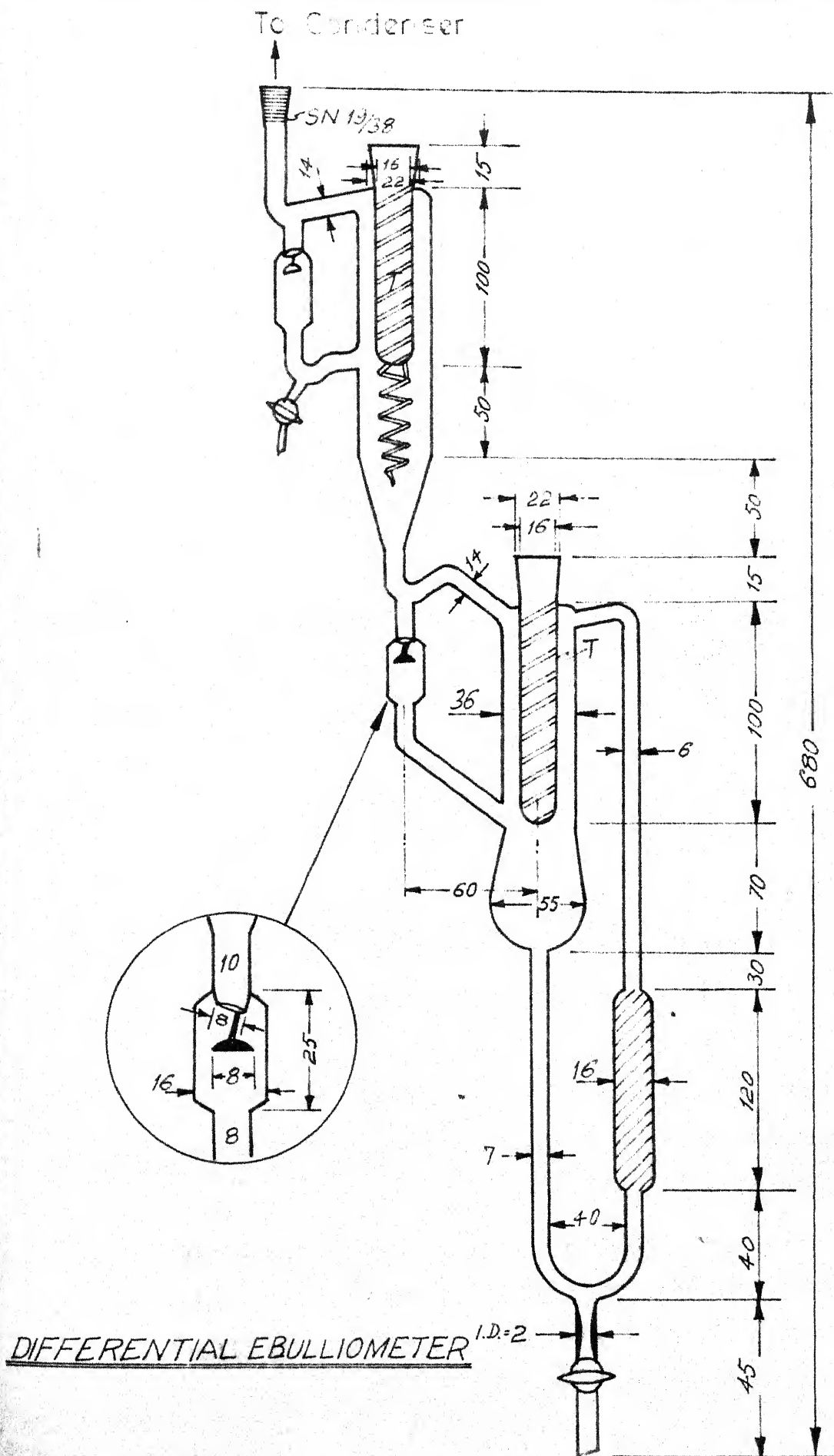


Fig. 6.

Rate of collection = 20 cc/hr.

Overall reflux ratio L/D = 2:1

Total amount charged = 1500 ml

Total amount recovered = 800 ml

% Recovery each time = 80 to 85%

Number of distillations
per formed = 4

Total time spent for
distillation = 200 hrs.

$$\Delta T = T_b - T_c$$

$$\begin{aligned} \Delta T \text{ of the original sample} &= 171.19 - 167.64 \\ &= 3.55^\circ\text{C} \end{aligned}$$

$$\begin{aligned} \Delta T \text{ after 1st distillation} &= 170.46 - 167.65 \\ &= 2.81^\circ\text{C} \end{aligned}$$

$$\begin{aligned} \Delta T \text{ after 2nd distillation} &= 169.83 - 167.64 \\ &= 2.19^\circ\text{C} \end{aligned}$$

$$\begin{aligned} \Delta T \text{ after 3rd distillation} &= 168.84 - 167.67 \\ &= 1.17^\circ\text{C} \end{aligned}$$

$$\begin{aligned} \Delta T \text{ after 4th distillation} &= 168.42 - 167.68 \\ &= .74^\circ\text{C} \end{aligned}$$

An essential difficulty that one faces in purifying methylcyclohexanol is that it forms 12 isomers (arising out of the combinations of ortho, meta and para positions with cis and trans conformations and dextro and levo rotatory behaviours). These isomers are spread over a large boiling range. Riedel boiling range is given as 165 - 173°C. It is not easy to

isolate these isomers just by distillation alone. Perfect control of pressure is also required Methylcyclohexane was also given an ebulliometric test. ΔT turned out to be negligible, less than $.1^{\circ}\text{C}$ which is the accuracy of measurement.

	Boiling Point in Differential Ebulliometer	Boiling point in Equilibrium still	Reported boiling point
$\text{C}_7\text{H}_{14}^{\text{O}}$	168.42	167.76	165.173°C (Riedel)
C_7H_{14}	100.90	100.71	100.90 ⁸

CHAPTER 4

EXPERIMENTAL RESULTS

The isobaric experimental data obtained for the system methylcyclohexanol-methylcyclohexane is reported in Table I. The smoothened data is reported in Table II. The accuracy of measurement of temperature is $\pm .1^{\circ}\text{C}$ and the accuracy of measurement of liquid and vapour composition is .0037. See Figure 7.

The smoothened data has been obtained by polynomial regression analysis of the experimental data. The degree of polynomial is chosen which satisfies the experimental data within 95% confidence limit and this optimum degree of the polynomial is obtained after applying F-test, on the experimental data.

When y is regressed on x the standard deviation is .006 when T is regressed on x the standard deviation is $.22^{\circ}\text{C}$. The accuracy of measurement of composition on a refractometer as obtained from calibration data is .0037; and the accuracy of temperature measurement by means of copper constantan thermocouple, as indicated by the analysis of calibration data is $.1^{\circ}\text{C}$. We observe that for both cases composition as well as temperature, error in the experiment is greater than the accuracy. This indicates that there are certain inherent drawbacks in the experimental set-up. The experimental errors incurred will then affect the analysis of the experimental results viz the calculation of activity coefficients of both the components - methylcyclohexanol and methylcyclohexane.

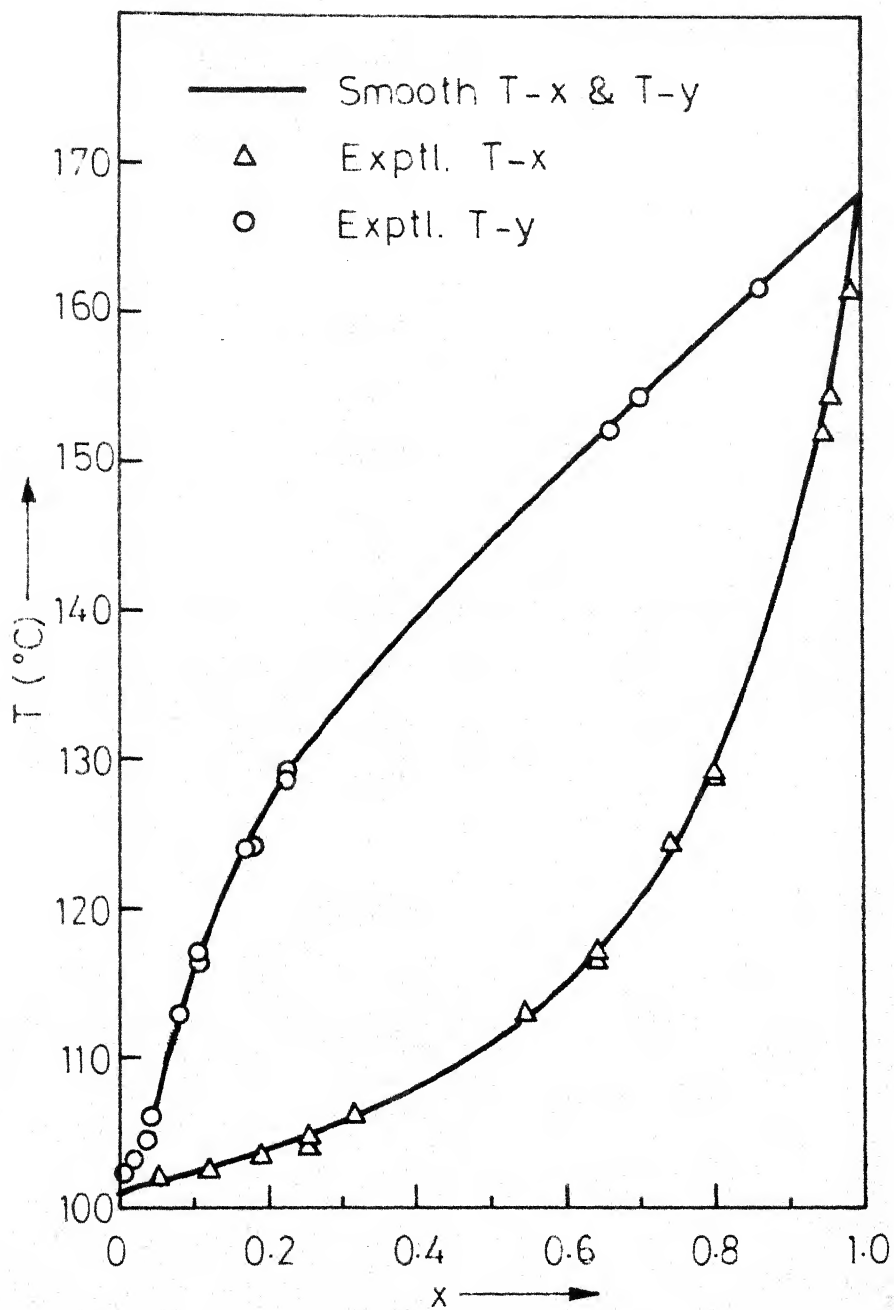


Fig. 7 - Vapor liquid equilibrium data for Methylcyclohexanol(1)-Methylcyclohexane(2) at 760mm Hg.

TABLE IEXPERIMENTAL RESULTS. $C_7H_{14}O - C_7H_{14}$ at 760 mm of Hg

X	Y	T °C
Pure component	-	
.0505	.0022	101.86
.1234	.0097	102.38
.1882	.0201	103.02
.2556	.0370	104.09
.2556	.0343	104.48
.3177	.0451	105.82
.5417	.0856	112.88
.5471	.0802	112.79
.6417	.1072	116.50
.6443	.1072	117.02
.7469	.1828	124.31
.7496	.1720	124.29
.8008	.2287	129.03
.8008	.2260	128.81
.9520	.6605	152.10
.9601	.7040	154.57
.9844	.8629	161.63
.9844	.8629	161.63
Pure component	-	167.76

TABLE II

SMOOTHENED RESULTS

 $C_7H_{14}O - C_7H_{14}$ at 760 mm of Hg.

X	Y	T°C
.0505	.0023	101.84
.1234	.0096	102.42
.1822	.0199	103.00
.2556	.0344	104.25
.3137	.0492	105.97
.5417	.0783	112.68
.5471	.0797	112.86
.6416	.1120	116.81
.6443	.1132	116.96
.7469	.1737	124.70
.7496	.1759	124.23
.8008	.2274	129.05
.9520	.6581	152.17
.9601	.7038	154.28
.9844	.8675	161.79

We shall now calculate the activity coefficients and also estimate the inherent error in their values resulting from the use of experimental data.

For calculation of the activity coefficients, the vapour phase in equilibrium with the non-ideal liquid phase has been assumed to be an ideal mixture of non ideal gases. The relevant equations for the activity coefficients will then be

$$\gamma_1 = \frac{Py_1}{P_1^0 x_1} \exp \left[\frac{(B_{11} - V_1^{OL})(P - P_1^0) + (2B_{12} - B_{11} - B_{22})y_2^2 P}{RT} \right] \quad (1)$$

$$\text{and } \gamma_2 = \frac{Py_2}{P_2^0 x_2} \exp \left[\frac{(B_{22} - V_2^{OL})(P - P_2^0) + (2B_{12} - B_{11} - B_{22})y_1^2 P}{RT} \right] \quad (2)$$

Equations (1) and (2) require, apart from T-x-y data (i) the isobaric pressure P, (ii) pure component vapour pressures which are estimated by the Martin equation for methylcyclohexanol and by Antoine equation for methylcyclohexane, (iii) second virial coefficients B_{11} and B_{22} which have been predicted by employing Kreglewski's double square well potential and (iv) the pure liquid molar volumes V_1^{OL} and V_2^{OL} calculated from the analytical expression given by Yen and Woods. This equation requires the values of critical compressibility, critical temperature T_c and critical volume V_c . These critical constants have been obtained from literature for methylcyclohexane and predicted for methylcyclohexanol.

The expression $2B_{12} - B_{11} - B_{22}$ has been assumed to be negligible compared to the other terms indicating that the

interaction virial coefficient is considered as an arithmetic mean of the pure component virial coefficients. This is the situation for an ideal mixture of nonideal gases where the equation of state for the nonideal gases can be given by the virial equation. Details regarding the use of pertinent equations for calculating the necessary information are being given below.

(i) Antoine equation⁹ for methylcyclohexane

$$\log_{10} P = A - B/(t+C) \quad (3)$$

Constants A, B and C have been obtained from literature.

(ii) Martin¹² equation for vapour pressure of methylcyclohexanol

$$\log_{10} P = A + B/T + CxT + DT^2 + ET^3 + F \log_{10}(G-T) \quad (4)$$

The constants have been obtained by fitting the experimental data collected by A. Mukherjee of our laboratory.

(iii) Kreglewski¹⁰ model gives the following equation for virial coefficients B_{11} and B_{22} .

$$\frac{B}{bV^*} = 1 - (R_1 - 1)(e^{-u/KT} - 1) - (R_2 - R_1)(e^{-su/KT} - 1) \quad (5)$$

Where R_1 and R_2 are given by the following expressions:

$$R_1 = \left[1 + \frac{S}{(V^*)^{1/3}} \right]^3 \quad (6)$$

$$R_2 = \left[1 + \left(\frac{V_0^*}{V^*} \right)^{1/3} \right]^3 \quad (7)$$

where V_0^* is the liquid molar volume of methane at reduced temperature = 0.6; S is a constant = .21 rounded off for all substances

and V^* is the liquid molar volume of the compound at $T_r = .6$.

The potential energy term u/kT is estimated by

$$-\frac{u}{kT} = \rho_c \frac{T_c}{T} \left(\frac{V^*}{V_0^*} \right)^{1/3} \quad (8)$$

ρ_c is the critical molar density, T_c the critical temperature and T is the temperature at which we wish to calculate the virial coefficient. The packing factor b is estimated by

$$b = .77 + .1325 (T_c)^{1/3} \quad (9)$$

The required values are ρ_c , T_c and V^* . For methyleyclohexane these have been obtained from the literature¹³ and for methyleyclohexanol they have been estimated.

(iii) Yen and Woods¹¹ equation for liquid molar volume

$$\rho_r = \frac{\rho}{\rho_c} = 1 + A (1-T_r)^{1/3} + B(1-T_r)^{2/3} + D(1-T_r)^{4/3} \quad (10)$$

ρ_r is the reduced molar density

T_r is the reduced temperature

ρ_c is the critical molar density

A, B and D are constants which are functions of critical compressibility alone.

Then

$$V^{\text{OL}}; \text{ the liquid molar volume is } = 1/(\rho_r \rho_c)$$

The critical constants for methyleyclohexanol have been estimated as follows:

(a) Critical Temperature:

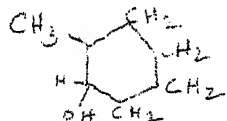
$$T_c = T_b \text{ (normal boiling point)} / \theta \quad (12)$$

where Lydersen's expression for θ is

$$\theta = .567 + \sum \Delta T - (\sum \Delta T)^2 \quad (13)$$

$\sum \Delta T$ is obtained by adding the atomic and structural contributions as listed in Table 2.2 of Sherwood and Reid "The Properties of Gases and Liquids".

Thus for methylcyclohexanol which ^{has} a structural formula of



$$\sum \Delta T = 4(-\text{CH}_2-) + 2(-\overset{|}{\text{CH}}) + \text{OH}- + \text{CH}_3-$$

in ring in ring in ring

$$= (4 \times .013) + (2 \times .012) + .082 + .020$$

$$= .052 + .024 + .082 + .02$$

$$= .178$$

$$\theta = .567 + .178 - (.178)^2 = .713$$

$$T_c = 441 / .713 = 620^\circ \text{K}$$

(b) Critical Volume:

Schuster's method has been adopted using the Lydersen's volume increments as tabulated in Table 2.12 of Sherwood and Reid. Errors of 2 to 5% are expected.

$$V_c = \sum \Delta V = \text{Base value} + (\text{CH}_3)-$$

$$+ 4(-\text{CH}_2-) + 2(-\overset{|}{\text{CH}}) + \text{OH}-$$

in ring in ring in ring

$$= 40 + 55 + (4 \times 44.5) + (2 \times 46) = 383 \text{ cc/g.mole}$$

(c) Critical Pressure:

Lydersen's method gives

$$P_c = \frac{M}{(\bar{\phi} + .34)^2} \quad (14)$$

where M = molecular weight = 114 for $C_7H_{14}O$ and $\bar{\phi}$ is additive constant which is determined from molecular structure contributions as given in Table 2.6 of Sherwood and Reid.

$$\begin{aligned} \bar{\phi} &= (CH_3-) + 2(-\overset{|}{\underset{|}{CH}}-) + 4(-CH_2-) + (OH-) \\ &= .227 + (2 \times .192) + (4 \times .184) + .06 \\ &= 1.407 \end{aligned}$$

$$\therefore P_c = \frac{114}{(1.407 + .34)^2} = 37.4 \text{ atm.}$$

Critical Compressibility Z_c

$$\begin{aligned} Z_c &= \frac{P_c V_c}{RT_c} \\ &= \frac{37.4 \times 383}{82.07 \times 620} = .281 \end{aligned} \quad (15)$$

Estimated virial coefficients of Methylcyclohexane are given in Table II and Methylcyclohexanol given in Table III. To obtain an analytical expression for the variation of the virial coefficient with temperature a polynomial of the form $a + bT + cT^2 + \dots$ has been fitted and the degree of polynomial is decided by subjecting it to F-test with 95% confidence limit.

TABLE III

VIRIAL COEFFICIENTS OF METHYLCYCLOHEXANE AND METHYLCYCLOHEXANOL

$$\left(\text{Using } -u/KT = \int_0^c \frac{T^c}{T} \times \frac{v^{*1/3}}{v_o^{*1/3}} \right.$$

$$b = .77 + .1325 (T_c)^{1/3}$$

in Kreglewski model)

T in °C	C ₇ H ₁₄ cc/g-mole	C ₇ H ₁₄ ^o cc/g-mole
373.16	-1501.56	-5787.34
378.16	-1446.27	-5550.97
383.16	-1394.19	-5329.89
388.16	-1345.07	-5122.50
393.16	-1298.67	-4927.90
398.16	-1254.78	-4744.94
403.16	-1213.22	-4572.69
408.16	-1173.81	-4410.28
413.16	-1136.39	-4256.94
418.16	-1100.83	-4111.98
423.16	-1067.00	-3974.77
428.16	-1034.77	-3844.74
433.16	-1004.04	-3721.36
438.16	-974.71	-3604.18
443.16	-946.70	-3492.75
448.16	-919.90	-3386.60
453.16	-894.26	-3285.61
458.16	-869.70	-3189.22

TABLE IVRELEVANT INFORMATION FOR CALCULATION OF
ACTIVITY COEFFICIENTS

Antoinne Constants for Methylcyclohexane:

$$A = 6.82689$$

$$B = 1272.864$$

$$C = 221.630$$

Martin Constants for Methylcyclohexanol:

$$A = 1.6235139$$

$$B = -943.73923$$

$$C = -.140738 \times 10^{-2}$$

$$D = .3470786 \times 10^{-4}$$

$$E = -.41477109 \times 10^{-7}$$

$$F = -.9089265$$

$$G = 627.98999$$

Critical Constants for Methylcyclohexane

$$Z_c = .251$$

$$T_c = 572.1^\circ\text{K}$$

$$V_c = 344 \text{ cc/g.mole}$$

Critical Constants (estimated) for Methylcyclohexanol:

$$Z_c = .281$$

$$T_c = 620^\circ\text{K}$$

$$V_c = 383 \text{ cc/g.mole}$$

$$P_c = 37.4 \text{ atm.}$$

(Table IV continued)

Coefficients in the polynomial fit for virial coefficient of C_7H_{14} which has a 5 degree polynomial

$$A = - .93186538 \times 10^5$$

$$B = + .91577548 \times 10^3$$

$$C = - .37652485 \times 10^1$$

$$D = + .79423174 \times 10^{-2}$$

$$E = - .85214885 \times 10^{-5}$$

$$F = + .37029944 \times 10^{-8}$$

Coefficient in the polynomial fit for virial coefficient of $C_7H_{14}O$ which has 3 degree polynomial:

$$A = -.98109325 \times 10^5$$

$$B = +.55025579 \times 10^3$$

$$C = -.10869500 \times 10^1$$

$$D = +.73802314 \times 10^{-3}$$

Expressions for Constants in Yen and Woods Equation:

$$A = 17.4425 - 214.578 Z_c + 989.629 Z_c^2 - 1522.06 Z_c^3$$

$$B = -3.28257 + 13.6377 Z_c + 107.4844 Z_c^2 - 384.2111 Z_c^3$$

$$\text{when } Z_c = .26$$

$$B = 60.2091 - 402.063 Z_c + 501.0 Z_c^2 + 641.0 Z_c^3$$

$$\text{when } Z_c = .26$$

$$D = 0.93 - B$$

Error Analysis:

As has been indicated earlier that vapour composition when regressed on liquid composition gives a standard deviation of .006 which is greater than .0037 the accuracy of measurement, and the equilibrium temperature T when regressed on x gives a standard deviation of .22°C which is again greater than .1°C the accuracy of measurement by copper-constantan thermocouple. Because of both these factors we keep the error in x as the fundamental error and the errors in y and T are dependent errors and are calculated as follows:

$$\Delta y = \frac{dy}{dx} \Delta x \quad (16)$$

$$\Delta T = \frac{dT}{dx} \Delta x \quad (17)$$

The derivatives $\frac{dy}{dx}$ and $\frac{dT}{dx}$ are obtained by differentiating the respective polynomial expressions for y and T . To give an idea of the errors in y and T these derivatives are being given in Table V. It is clear from the table that because of steep ascent in the pure region of methylcyclohexanol errors incurred will be more. The errors so incurred will affect the calculation of the activity coefficients. It is our aim now to analyze the method of error propagation and see how ultimately they are reflected in $\ln \gamma_1$, $\ln \gamma_2$ and $\ln \gamma_1/\gamma_2$.

According to the general formula of errors if we have a quantity N given by

$$N = f(u_1, u_2, \dots, u_k) \quad (18)$$

then ΔN the absolute error in N is given by

TABLE V

DERIVATIVES OF VAPOUR COMPOSITIONS AND
EQUILIBRIUM TEMPERATURE WITH RESPECT TO
LIQUID COMPOSITION

x	$\frac{dy}{dx}$	$\frac{dT}{dx}$
0.0505	0.0606	8.1411
0.1234	0.1309	7.2224
0.1882	0.1865	12.8155
0.2556	0.2443	23.7648
0.3177	0.1991	28.3267
0.5417	0.2531	33.2051
0.5471	0.2639	33.4912
0.6416	0.4415	55.1234
0.6443	0.4468	55.8951
0.7469	0.8069	84.6485
0.7496	0.8229	85.7489
0.8008	1.2148	99.7107
0.9520	5.4226	251.1919
0.9601	5.8923	271.4175
0.9844	7.5809	346.6897

$$\Delta N = \frac{\partial f}{\partial u_1} \Delta u_1 + \frac{\partial f}{\partial u_2} \Delta u_2 + \dots + \frac{\partial f}{\partial u_k} \Delta u_k$$

And since these errors can act in opposite directions one must take the absolute of the errors contributed by each independent variable.

$$\Delta N = \left| \frac{\partial f}{\partial u_1} \Delta u_1 \right| + \left| \frac{\partial f}{\partial u_2} \Delta u_2 \right| + \dots + \left| \frac{\partial f}{\partial u_k} \Delta u_k \right| \quad (19)$$

$$\text{So that for } \gamma_1 = \frac{P y_1}{P_1^0 x_1 \exp u_1} \quad (20)$$

$$\Delta (\ln \gamma_1) = \frac{\Delta \gamma_1}{\gamma_1} \quad (21)$$

$$= \left| \frac{\Delta y}{y_1} \right| + \left| \frac{\Delta P}{P} \right| + \left| \frac{\Delta x}{x_1} \right| + \left| \frac{\Delta P_1^0}{P_1^0} \right| \quad (22)$$

neglecting the error in the non-ideal term $\exp u_1$. Δy is obtained from equation (16). ΔP is the error in measurement of total pressure which directly depends on the error incurred in measurement of ebulliometric temperature of the reference liquid benzene. Corresponding to $\pm 1^\circ\text{C}$ at normal boiling point of benzene $\Delta P = \pm 2.14$ mm.

$$\Delta P_1^0 = \frac{dP_1^0}{dT} \Delta T$$

Since P_1^0 corresponds to methylcyclohexanol the derivative is obtained by differentiating Martin equation with respect to temperature. ΔT is obtained from equation (17).

A similar analysis for error in $\Delta (\ln \gamma_2)$ is adopted except that now $\frac{dP_2^0}{dT}$ is obtained by differentiating the Antoine equation.

Since $\ln \frac{\gamma_1}{\gamma_2} = \ln \gamma_1 - \ln \gamma_2$
 absolute error in $\ln \frac{\gamma_1}{\gamma_2}$ is given by

$$\Delta \left(\ln \frac{\gamma_1}{\gamma_2} \right) = \left| \Delta (\ln \gamma_1) \right| + \left| \Delta (\ln \gamma_2) \right|$$

The values of $\ln \gamma_1$, $\ln \gamma_2$ and $\ln \gamma_1 / \gamma_2$ calculated from experimental data are reported in Table VI, along with errors incurred in each. See Figure 8.

TABLE VI

LOG OF ACTIVITY COEFFICIENTS AND
LOG OF RATIO OF ACTIVITY COEFFICIENTS

x_1	$\ln \gamma_1$	$\Delta(\ln \gamma_1)$	$\ln \gamma_2$	$\Delta(\ln \gamma_2)$	$\ln \gamma_1/\gamma_2$	$\Delta(\ln \gamma_1/\gamma_2)$
0.0505	-1.1566	0.1833	0.0254	+ 0.0070	-1.1819	0.1903
0.1234	-0.6402	0.0833	0.0826	0.0076	-0.7228	0.0909
0.1882	-0.3523	0.0572	0.1336	0.0082	-0.4860	0.0654
0.2556	-0.1519	0.3436	0.1726	0.0088	-0.3246	0.0524
0.3177	-0.0056	0.3295	0.2012	0.0091	-0.2668	0.0336
0.3417	-0.3515	0.3217	0.3972	0.0120	-0.7487	0.0337
0.3471	-0.3494	0.0219	0.4031	0.0121	-0.7524	0.0340
0.4416	-0.2926	0.0232	0.5052	0.0151	-0.7978	0.0363
0.4443	-0.2908	0.0232	0.5078	0.0152	-0.7987	0.0384
0.7469	-0.2271	0.0250	0.6124	0.0211	-0.8395	0.0462
0.7496	-0.2251	0.0251	0.6152	0.0214	-0.8403	0.0465
0.8008	-0.1793	0.0273	0.6708	0.0273	-0.8501	0.0546
0.9520	0.0551	0.0373	0.8020	0.1387	-0.7469	0.1759
0.9601	0.0573	0.0377	0.8033	0.1692	-0.7459	0.2070
0.9844	0.0454	0.0390	0.7994	0.4518	-0.7540	0.4903

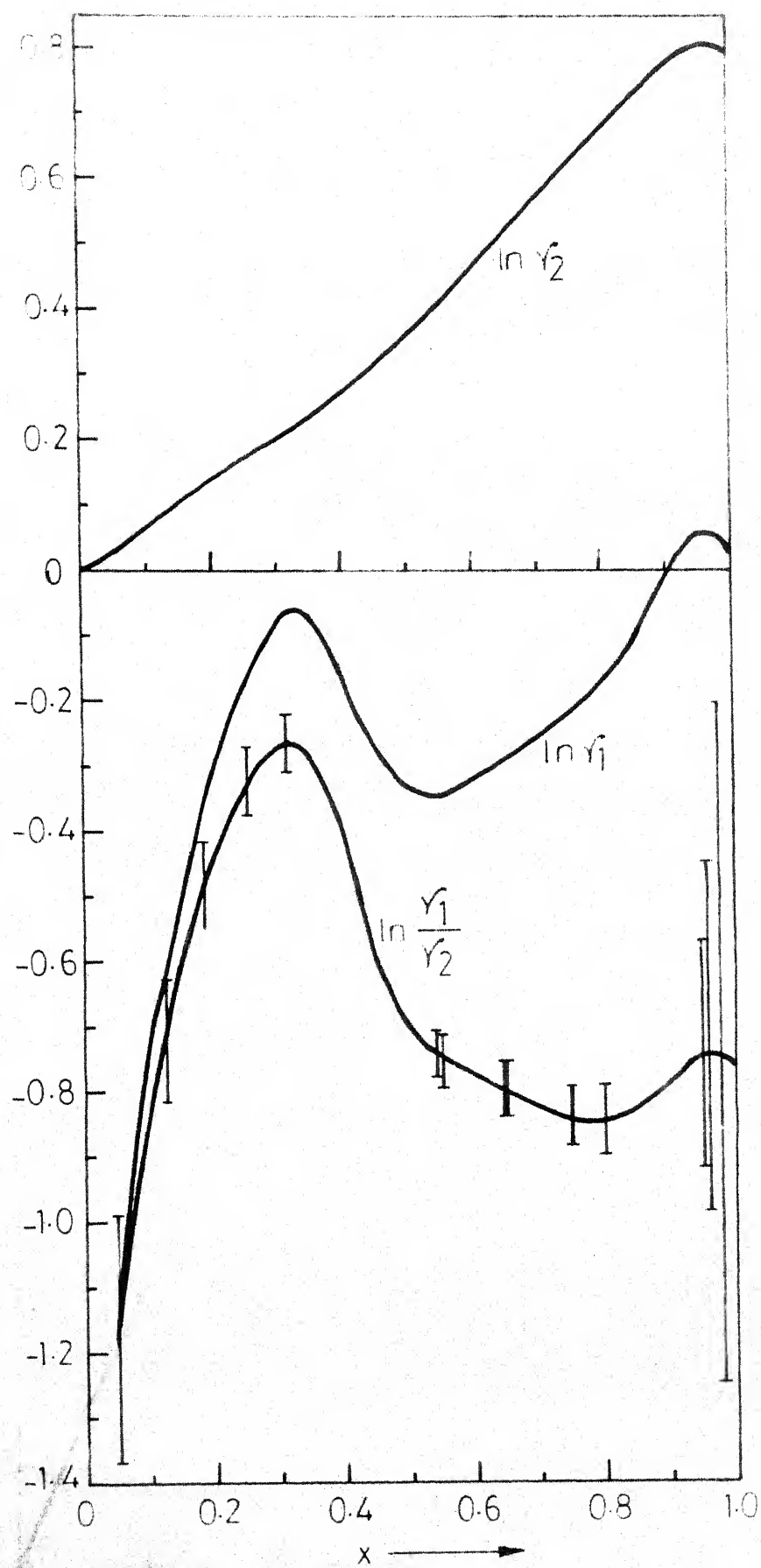


Fig. 8 - Plot of the log of activity coefficients for
Methylcyclohexanol(1) - Methylcyclohexane
at 760 mm of Hg.

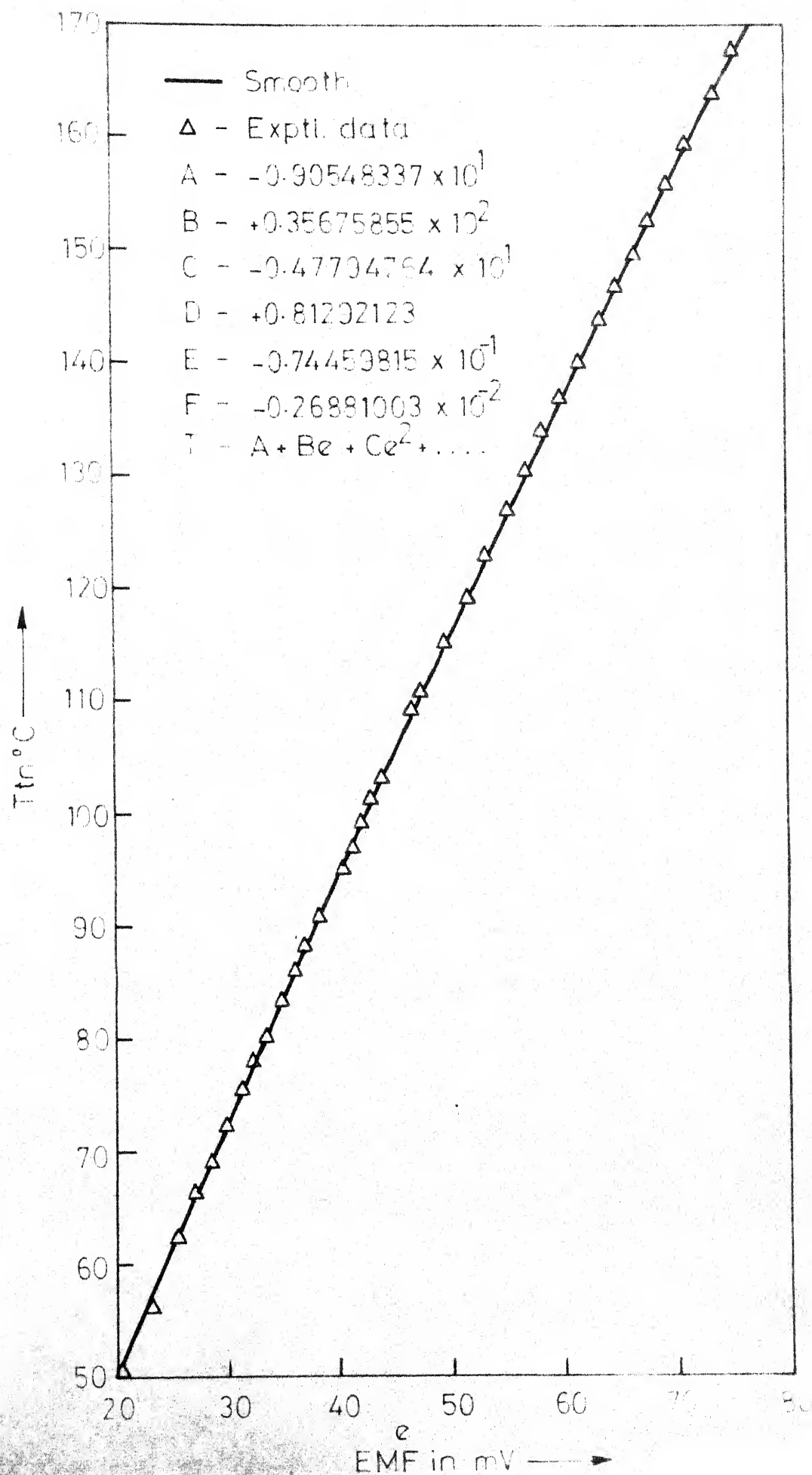


Fig. 9 - Calibration curve for copper

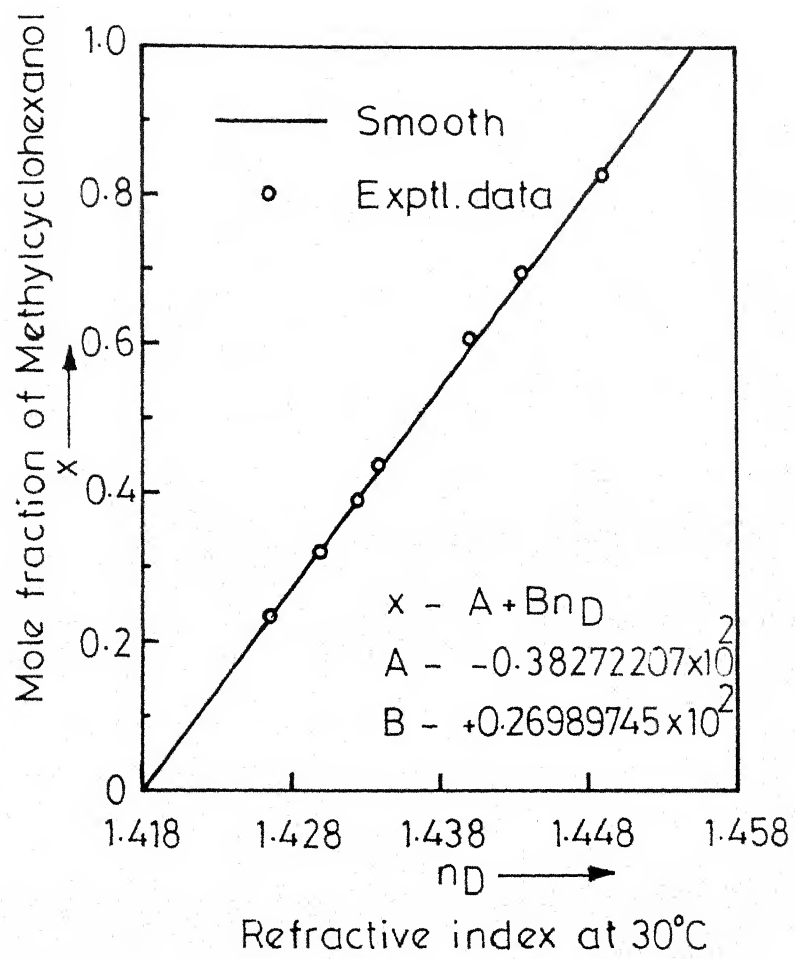


Fig.10 - Calibration curve for refractometer.

CHAPTER 5

THERMODYNAMIC CONSISTENCY TEST

The Gibbs-Duhem equation interrelates activity coefficient⁺ of all components in mixture. Therefore, activity coefficients calculated from thermodynamically consistent experimental data should obey the Gibbs-Duhem equation. If they do not then it is concluded that the data are not thermodynamically consistent. This logic is the basis of all thermodynamic consistency tests.

The Gibbs Duhem equation for the binary isobaric data is given as

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} + \frac{h^E}{RT^2} \frac{dT}{dx_1} = 0 \quad (1)$$

This indicates that in addition to activity coefficient data one needs the excess heat of mixing data also. This is a serious limitation since the excess heat of mixing data are rarely available, but it is a limitation which is unavoidable and pertains to all tests for thermodynamic consistency. Therefore, at best the test can only be approximate. Herrington has given a semi-empirical test for isobaric data and the heart of it lies in an estimation of the last term in the above equation.

Integral or area test of Redlich-Kister and Herrington:

This approach tests the data as a whole rather than point by point and it has the important advantage that it can be easily carried out quantitatively.

$$\frac{g^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (2)$$

Differentiating equation (2)

$$\begin{aligned} \frac{d(g^E/RT)}{dx_1} &= x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} + \ln \gamma_1 - \ln \gamma_2 \\ &= \ln \frac{\gamma_1}{\gamma_2} - \frac{h^E}{RT^2} \frac{dT}{dx_1} \end{aligned} \quad (3)$$

On integration of equation (3)

$$\begin{aligned} \int_0^1 \frac{d(g^E/RT)}{dx_1} dx_1 &= \int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 - \int_0^1 \frac{h^E}{RT^2} dT \\ &= \left. \frac{g^E}{RT} \right|_{x_1=1} - \left. \frac{g^E}{RT} \right|_{x_1=0} = 0 \end{aligned} \quad (4)$$

Since excess free energies for pure components are necessarily zero.

Therefore if one plots $\ln \frac{\gamma_1}{\gamma_2}$ vs x_1 and neglects the heat of mixing term then the area under the curve should be zero.

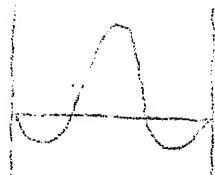
For the experimental data obtained for the system methylcyclohexanol - methylcyclohexane the area is negative, (Figure 8). It makes no attempt to equalize to zero. In such a case even applying Herrington's test has no validity because the factor D which is defined as

$$D = 100 \times \frac{\text{area above x-axis} - \text{area below x-axis}}{\text{area above x-axis} + \text{area below x-axis}}$$

turns out to be negative, equal to -100.

Actually for hydrocarbon-alcohol systems the g^E function behaves irregularly like for Benzene-BuOH system it behaves as

shown below:

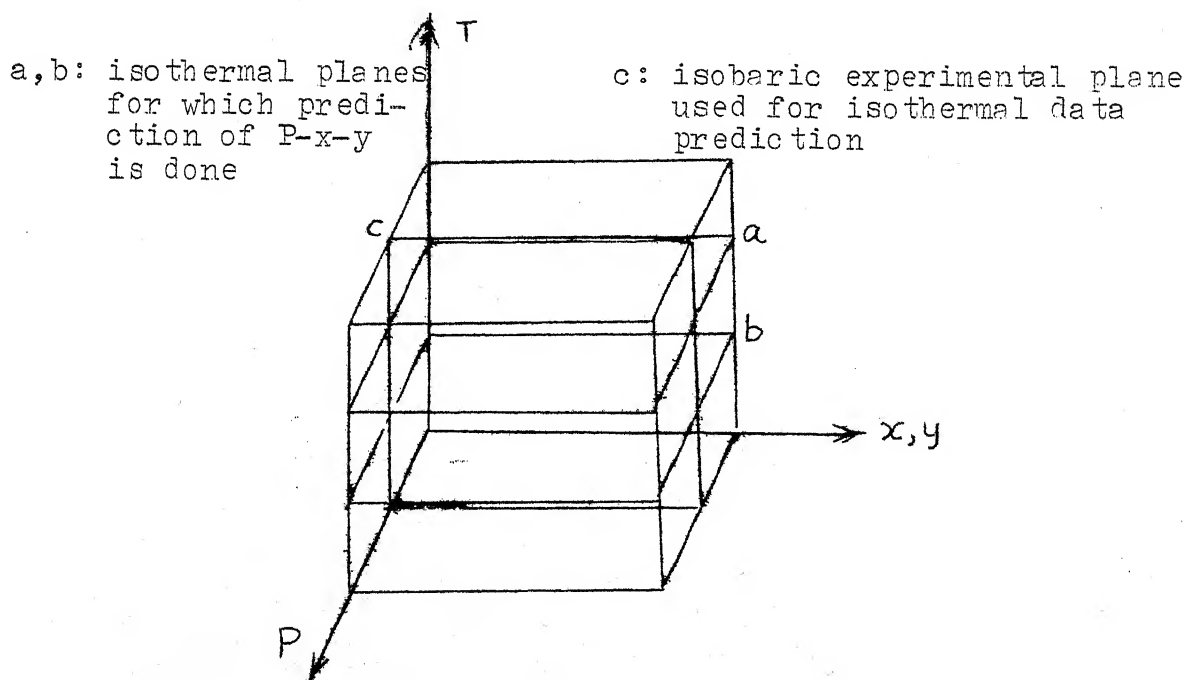


One can then imagine the behaviour of h^E which has more assymetry than g^E . It is likely that h^E for methylcyclohexanol - methylcyclohexane system is highly assymetrical and irregular. Therefore in the absence of h^E data our test for thermodynamic consistency is not valid.

THEORETICAL ANALYSIS

In our experiment we have collected isobaric data for the system methylcyclohexanol-methylcyclohexane at 760 mm Hg. How does this data lend itself to an insight into the behavior of liquid mixtures? At first glance it does not offer us much hope for isobaric data is directly useful in design of distillation units and it is the isothermal data which offers a chance for direct study on the behaviour of liquid mixtures. This isothermal data is more difficult to collect experimentally. Can we then predict the isothermal data from the isobaric data?

This is a weighty question with profound implications. If we can, then we can predict P - x - y at different temperatures thus gathering information for all P - T - x - y . Let us form an image of what this means.



The answer to such an interesting question is in the positive, and it covers zeotropes as well as azeotropes.

The structure of our prediction of isothermal vapour liquid equilibrium is built on the Redlich-Kister expression for excess free energy, which is based on the conformal solution theory.

$$g^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots] \quad (1)$$

With B and C equal to zero, the expression for g^E is the same as given by regular solution theory. For strictly regular solutions the constant A is independent of temperature and S^E , the excess entropy of mixing, is zero and h^E , the excess heat of mixing, equal to g^E . However the available experimental data shows that S^E is not necessarily zero and h^E has more asymmetry than g^E . This indicates that A is not independent of temperature. Same reasoning would then apply for the higher constants in the Redlich-Kister expression.

It was Haase, who first found the temperature dependence of constants A and B for cyclohexane-Methanol system. The experimental curve of g^E for this system is represented by the equation

$$g^E = x_1 x_2 (A + Bx_2^2) \quad (2)$$

in which A and B are the following functions of the temperature

$$A = 2070 - 1.85 T \quad (3)$$

$$B = -3107 + 10T \quad (4)$$

Haase then used these equations to compute S^E and h^E . However,

we can use the above explicit forms of A and B for our purpose of predicting the isothermal data. Calculate A and B at different temperatures and plug the obtained values in equation (2). From the expression of g^E one can obtain the activity coefficients which can be used to predict P-x and y-x curves at the chosen temperature. The problem then essentially boils down to the determination of temperature dependence of the constants. This procedure is intricate and we shall develop the theory bit by bit.

Malesinski has employed the regular solution theory i.e. $g^E = Ax_1x_2$ and assumed A as independent of temperature. The value of the constant A has been determined from one experimental T-x data at $x = .5$. This value of A has then been used to predict isobaric data over the whole range of concentration. Satisfactory results have been achieved by him for systems like methanol-acetone, chloroform-acetone, heptane-benzene.

However, the value of A can be improved by a process of successive approximations. If we take T_{exptl} as a function of A and expand it by Taylor's series about the point T_{calc} then

$$T_{\text{exptl}} = T_{\text{calc}} + \frac{dT}{dA} \delta A + \frac{d^2T}{dA^2} \delta A^2 + \dots$$

or $\Delta T = T_{\text{exptl}} - T_{\text{calc}} = \frac{dT}{dA} \delta A$, truncating the higher derivatives

The aim is to reduce the error in ΔT by the least squares technique. Application of the least squares method will give δA , the incremental value in A. A now alters to $A + \delta A$. With this

new value of A , T_{calc} over the whole range is again obtained. In this manner, one can iteratively improve T_{calc} and reduce the error in T i.e. $(T_{\text{calc}} - T_{\text{exptl}})$. However a stage will be reached when no improvement is possible, and yet T_{calc} deviates largely from T_{exptl} , for we are still essentially dealing with one constant for expressing g^E for a strictly regular solution, which is a symmetric curve for g^E when plotted as a function of composition.

This is the stage when we must incorporate more number of constants in the expression for g^E . We can do this in two different ways - (i) make B & C in equation (1) non-zero retaining their temperature independence or (ii) make A dependent on temperature, this dependence may be linear or quadratic to fit the experimental data, and keep B and C zero. Once these temperature dependent constants are obtained we can employ them for isothermal prediction.

Let us now proceed to obtain T - x and y - x .

The equations for the isobaric vapour-liquid equilibrium when a real liquid solution is in equilibrium with an ideal vapour are

$$Py_1 = P_1^0 x_1 \gamma_1 \quad (5)$$

$$Py_2 = P_2^0 x_2 \gamma_2 \quad (6)$$

The equation for the boiling temperature isobar is obtained by adding (5) and (6) and dividing by the total pressure P .

$$\text{i.e.} \quad \sum x_i \gamma_i = 1 \quad (7)$$

where $\lambda_i = \frac{\text{Vapour Pressure of } i \text{ at Temperature } T}{\text{Total Pressure}}$

The equation for the vapor composition in terms of liquid composition will then be

$$y_r = \frac{\lambda_r x_r \gamma_r}{\sum \lambda_i x_i \gamma_i} \quad (8)$$

The activity coefficients appearing in equations (7) and (8) are obtained from the following relation

$$\ln f_i = \frac{1}{RT} \mu_i^E = \frac{1}{RT} \frac{\partial (n_T g^E)}{\partial n_i}, \quad n_T = \sum n_i \quad (9)$$

Equation (7) is implicit in T and it does not lend itself to easy calculation of T . This difficulty can be overcome by using another form of the equation for the boiling temperature isobar, which can be derived by using the excess free energy of mixing. Moreover at this point we wish to incorporate the non-ideality in the vapour phase also. So that

$$P y_1 = P_1^0 x_1 \gamma_1 \exp \frac{(V_1^{OL} - B_{11})(P - P_1^0) - \delta_{12} y_2^2 P}{RT} \quad (10)$$

$$\text{and } P y_2 = P_2^0 x_2 \gamma_2 \exp \frac{(V_2^{OL} - B_{22})(P - P_2^0) - \delta_{12} y_2^2 P}{RT} \quad (11)$$

$$\text{or } P y_1 = P_1^0 x_1 \gamma_1 \exp u_1 \quad (12)$$

$$\text{and } P y_2 = P_2^0 x_2 \gamma_2 \exp u_2 \quad (13)$$

$$\text{where } u_1 = \frac{(V_1^{OL} - B_{11})(P - P_1^0) - \delta_{12} y_2^2 P}{RT}$$

$$u_2 = \frac{(V_2^{OL} - B_{22})(P - P_2^0) - \delta_{12} y_1^2 P}{RT}$$

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$$\delta_{12} = 2B_{12} - B_{11} - B_{22}.$$

The excess free energy of mixing is given by

$$g^E = RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (14)$$

Using equations (12) and (13)

$$\begin{aligned} g^E &= RT \left[(x_1 \ln \frac{Py_1}{P_1^0 x_1 \exp u_1} + x_2 \ln \frac{Py_2}{P_2^0 x_2 \exp u_2}) \right] \\ &= RT \left[(x_1 \ln \frac{P}{P_1^0} + x_2 \ln \frac{P}{P_2^0} + x_1 \ln \frac{y_1}{x_1} \right. \\ &\quad \left. + x_2 \ln \frac{y_2}{x_2} - x_1 u_1 - x_2 u_2) \right] \end{aligned} \quad (15)$$

$$\text{or} \quad g^E = RT (v + w - u) \quad (16)$$

where v , w and u are defined as

$$v = x_1 \ln \frac{P}{P_1^0} + x_2 \ln \frac{P}{P_2^0} \quad (17a)$$

$$w = x_1 \ln \frac{y_1}{x_1} + x_2 \ln \frac{y_2}{x_2} \quad (17b)$$

$$u = x_1 u_1 + x_2 u_2 \quad (17c)$$

From equation (16)

$$T = \frac{g^E}{R(v + w - u)} \quad (18)$$

If the theoretical expression for g^E is fixed the above equation can be used to obtain T . Equation (18) though implicit in T like equation (7) is not as unwieldy and T can be improved iteratively with the first approximation on the right hand side taken as $T = T_1 x_1 + T_2 x_2$.

However equation (18) belies the trust put in it. Computer calculations revealed that v is very sensitive to temperature and even a little off approximation for T on the right hand side makes the expression $(v + w - u)$ negative. With the result that one obtains negative temperatures. To counteract this problem and make the iterations converge we had to express the term v differently.

From Claussius-Clapeyron equation, we have

$$RT \ln \frac{P}{P_i^0} = \Delta S_i (T_i - T) \quad (19)$$

if we assume the molar heat of vaporization to be constant over the temperature interval in question. Here T_i is the pure component boiling point at pressure P and ΔS_i is the entropy of vaporization. Plugging this relation in equation (16) one obtains

$$g^E = x_1 \Delta S_1 (T_1 - T) + x_2 \Delta S_2 (T_2 - T) + RTw - RTu \quad (20)$$

Transforming the above relation

$$T = T_1 x_1 \frac{\Delta S_1}{\Delta S_0} + T_2 x_2 \frac{\Delta S_2}{\Delta S_0} - \frac{g^E}{\Delta S_0} + \frac{RTw}{\Delta S_0} - \frac{RTu}{\Delta S_0} \quad (21)$$

where $\Delta S_0 = x_1 \Delta S_1 + x_2 \Delta S_2$

It is this equation which we are going to use for getting the T - x relation. The first approximation for T is again $T_1 x_1 + T_2 x_2$. The entropies are calculated from equation (19), g^E is given by Redlich-Kister expression, u is the expression for non-ideality of the vapor phase. It is the term w which has to be made more explicit.

$$w = x_1 \ln \frac{y_1}{x_1} + x_2 \ln \frac{y_2}{x_2}$$

In terms of relative volatility α_{21}

$$\frac{y_1}{x_1} = \frac{1}{x_1 + x_2 \alpha_{21}}$$

$$\frac{y_2}{x_2} = \frac{x_2 \alpha_{21}}{x_1 + x_2 \alpha_{21}}$$

$$\begin{aligned} \therefore w &= x_1 \ln \left[1 + x_2 (\alpha_{21} - 1) \right] - x_2 \ln \left[1 + x_2 (\alpha_{21} - 1) \right] \\ &\quad + x_2 \ln \alpha_{21} \\ &= x_2 \ln \alpha_{21} - \ln \left[1 + x_2 (\alpha_{21} - 1) \right] \end{aligned} \quad (22)$$

where the relative volatility α_{21} is defined as

$$\alpha_{21} = \frac{y_2/x_2}{y_1/x_1} = \frac{P_2^0 r_2 \exp u_2}{P_1^0 r_1 \exp u_1} \quad (23)$$

$$\begin{aligned} \text{and } \ln \alpha_{21} &= \ln \frac{P_2^0}{P_1^0} + \ln \frac{r_2}{r_1} + u_2 - u_1 \\ &= \frac{\Delta S_2}{RT} (T - T_2) - \frac{\Delta S_1}{RT} (T - T_1) + \frac{1}{RT} \frac{\partial g^E}{\partial x_2} + (u_2 - u_1) \end{aligned} \quad (24)$$

w as a function of $\ln \alpha_{21}$ alone is given by

$$\begin{aligned} w &= -x_1 x_2 (\ln \alpha_{21})^2 + x_1 x_2 \frac{(x_1 - x_2)}{6} (\ln \alpha_{21})^3 \\ &\quad + \frac{x_1 x_2}{24} (1 - 6x_1 x_2) (\ln \alpha_{21})^4 + x_1 x_2 (x_1 - x_2) \\ &\quad \frac{(1 - 12x_1 x_2)}{120} (\ln \alpha_{21})^5 + \frac{x_1 x_2}{720} (1 - 30x_1 x_2) \\ &\quad + 120x_1^2 x_2^2 (\ln \alpha_{21})^6 + \dots \end{aligned} \quad (25)$$

Having obtained the T-x relation, we can also obtain y-x from equation (8),

$$\text{where } \lambda_i = \frac{P_i^0}{P} \exp u_i$$

Having obtained a useful form of equation for T, which poses no convergence problems, we now proceed to our main objective of obtaining the constants in the Redlich-Kister equation. We shall consider the general case of quadratic temperature dependence of the first two constants A and B.

$$A = C_1 + C_2 T + C_3 T^2 \quad (26a)$$

$$B = C_4 + C_5 T + C_6 T^2 \quad (26b)$$

so that

$$g^E = (C_1 + C_2 T + C_3 T^2) x_1 x_2 + (C_4 + C_5 T + C_6 T^2) x_1 x_2 (x_1 - x_2). \quad (27)$$

Particular case of Malesinski's prediction:

$$g^E = C_1 x_1 x_2 \quad (28)$$

C_1 is obtained from the experimental point at $x = .5$. Only temperature value is needed, not the vapour composition. And since Malesinski has neglected the non-ideality of the vapour phase the term u in equation (16) is neglected. From equation (16) in conjunction with equation (28)

$$C_1 = 4RT^* (v^* + w^*) \quad (29)$$

* indicates that the values v and w are calculated at temperature T^* corresponding to $x = .5$. Since Malesinski makes no attempt to improve the value of this constant C_1 , no least square analysis is

required. And therefore one essentially obtains predicted (T-x) curve employing equation (21) with u term equal to zero and predicted (y-x) from equation (8).

More than one constant with temperature dependence included*.

$$\bar{C} = (C_1 \ C_2 \ C_3 \ C_4 \ C_5 \ C_6) \quad (30)$$

We will determine the elements in this linear vector \bar{C} by least square analysis, and the values are improved iteratively. To find a first approximation we assume that the solution behaves like a regular solution, so that only C_1 is non-zero. C_1 is evaluated at equimolar concentration for the working of the least square technique (T-x) experimental data are required.

$$C_1 = 4RT^* (v^* + w^* - u^*) \quad (31)$$

T is calculated for the experimental liquid compositions using equation (21). First approximation for $T = T_1 x_1 + T_2 x_2$. Equation (21) is used iteratively at each liquid composition till no further improvement in value of T is possible. Then the temperature residual $\Delta T = T_{\text{calc}} - T_{\text{exptl}}$ is calculated for each data point.

ΔT is a function of the elements in \bar{C} . By a Taylor series expansion of T_{exptl} about T_{calc} we have

$$T_{\text{exptl}} = T_{\text{calc}} + \sum_{i=1}^M \frac{\partial T}{\partial C_i} \delta C_i + \text{Higher derivatives.}$$

We shall neglect the higher derivatives and then

$$\Delta T = \sum_{i=1}^M \frac{\partial T}{\partial C_i} \delta C_i, \quad M \text{ is the no. of elements in } \bar{C}. \quad (33)$$

The first derivatives of T with respect to elements in \bar{C} are obtained as shown below.

Let us say that

$$T = f(T, C_i) \quad i = 1 \text{ to } M \quad (34)$$

$$\text{Then } df = \frac{\partial f}{\partial T} dT + \frac{\partial f}{\partial C_i} dC_i$$

$$\text{and } \frac{dT}{dC_i} = \frac{df}{dC_i} = \frac{\partial f}{\partial T} \frac{dT}{dC_i} + \frac{\partial f}{\partial C_i}, \quad \frac{dC_j}{dC_i} = 0 \quad \text{for } j \neq i \quad (35)$$

$$\therefore \frac{dT}{dC_i} = \frac{\partial f / \partial C_i}{(1 - \frac{\partial f}{\partial T})} \quad (36)$$

where f is given by equation (21).

In equation (36) we have yet ^{to} analyse the partial derivatives $\frac{\partial f}{\partial C_i}$ and $\frac{\partial f}{\partial T}$. We shall now present the analysis for these partial derivatives.

Analysis for $\frac{\partial f}{\partial T}$: Taking the derivative of equation (21).

$$\begin{aligned} \frac{\partial f}{\partial T} = & \left[T_1 x_1 \frac{\partial \Delta S_1}{\partial T} + T_2 x_2 \frac{d \Delta S_2}{dT} - \frac{\partial g^E}{\partial T} \right. \\ & \left. + RT \left(\frac{\partial w}{\partial T} - \frac{\partial u}{\partial T} \right) + R(w-u) \right] / \Delta S_0 - \frac{T}{\Delta S_0} \frac{d \Delta S_0}{dT} \end{aligned} \quad (37)$$

$$\frac{d \Delta S_1^0}{dT} = \frac{1}{(T_1 - T)} \left[R \ln \frac{P}{P_1^0} - RT \frac{d \ln P_1^0}{dT} + \Delta S_1 \right] \quad (38a)$$

a similar equation will be obtained for the second component.

For $\frac{d \ln P_i^0}{dT}$ we employ usually the Antoine equation.

$$\frac{d \Delta S_0}{dT} = x_1 \frac{d \Delta S_1^0}{dT} + x_2 \frac{d \Delta S_2^0}{dT} \quad (38b)$$

From equation (27)

$$\frac{\partial u^E}{\partial T} = (C_2 + 2C_3 T) x_1 x_2 + (C_5 + 2C_6 T) x_1 x_2 (x_1 - x_2) \quad (38c)$$

The temperature derivatives of the term u are intricate.

$$\frac{\partial u}{\partial T} = x_1 \frac{\partial u_1}{\partial T} + x_2 \frac{\partial u_2}{\partial T} \quad (38d)$$

$$u_i = \frac{(V_i^{OL} - B_{ii})(P - P_i^0) - \delta_{12} y_j^2}{RT}$$

In the above expression liquid molar volume, virial coefficient, vapour pressure of pure component i , y_i are all temperature dependent. We shall neglect the temperature dependence of δ_{12} .

From the expressions of vapour compositions y_1 and y_2 in terms of the relative volatility α_{21} we have

$$\frac{dy_2}{dT} = \frac{y_2 y_1}{\alpha_{21}} \frac{d\alpha_{21}}{dT} \quad (38e)$$

$$\frac{dy_1}{dT} = -y_1^2 \frac{x_2}{x_1} \frac{d\alpha_{21}}{dT} \quad (38f)$$

Using equations (38e) and (38f) we get

$$\frac{\partial u_1}{\partial T} = -\frac{u_1}{T} + \left(\frac{dV_1^{OL}}{dT} - \frac{dB_{11}}{dT} \right) (P - P_1)/RT \quad (38g)$$

$$- \left(\frac{V_1 - B_{11}}{RT} \right) \frac{dP_1^0}{dT} - 2P \delta_{12} \frac{y_2^2 y_1}{21} \frac{\partial \alpha_{21}}{\partial T} / RT$$

$$\frac{\partial u_2}{\partial T} = \frac{u_2}{T} + \left(\frac{dV_2^{OL}}{dT} - \frac{dB_{22}}{dT} \right) (P - P_2^0)/RT$$

$$- \frac{(V_2^{OL} - B_{22})}{RT} \frac{dP_2^0}{dT} + \frac{2P \delta_{12}}{RT} y_1^3 \frac{x_2}{x_1} \frac{d\alpha_{21}}{dT} \quad (38h)$$

From equation (24)

$$\begin{aligned} \frac{\partial \alpha_{21}}{\partial T} &= \alpha_{21} \frac{\ln \dot{\partial}_{21}}{\partial T} \\ &= \alpha_{21} \left[\frac{d \ln P_2^0}{dT} - \frac{d \ln P_1^0}{dT} - \frac{1}{RT^2} \frac{\partial g^E}{\partial x_2} + \frac{1}{RT} \frac{d}{dT} \left(\frac{\partial g^E}{\partial x_2} \right) \right. \\ &\quad \left. + \frac{\partial u_2}{\partial T} - \frac{\partial u_1}{\partial T} \right] \end{aligned} \quad (38i)$$

Equations (38g), (38h) and (38i) can be solved simultaneously to get explicit relations for

$$\frac{\partial u_2}{\partial T}, \frac{\partial u_1}{\partial T} \text{ and } \frac{\partial \alpha_{21}}{\partial T}$$

From equation (24) we get the expression for $\frac{\partial w}{\partial T}$

$$\begin{aligned} \frac{\partial w}{\partial T} &= -x_1 x_2 \left[2 \ln \alpha_{21} + \frac{(x_1 - x_2)}{2} (\ln \alpha_{21})^2 \right. \\ &\quad + \frac{(1 - 6x_1 x_2)}{6} (\ln \alpha_{21})^3 + \frac{(x_1 - x_2)(1 - 12x_1 x_2)}{24} (\ln \alpha_{21})^4 \\ &\quad \left. + \frac{1 - 30x_1 x_2 + 120x_1^2 x_2^2}{120} (\ln \alpha_{21})^5 + \dots \right] \frac{1}{\alpha_{21}} \frac{\partial \alpha_{21}}{\partial T} \end{aligned} \quad (38j)$$

Analysis for $\partial f / \partial C_i$:

Taking the derivative of f with respect to constant C_i

$$\frac{\partial f}{\partial C_i} = -\frac{1}{\Delta S_0} \frac{\partial g^E}{\partial C_i} + \frac{RT}{\Delta S_0} \frac{\partial w}{\partial C_i} - \frac{RT}{\Delta S_0} \frac{\partial u}{\partial C_i} \quad (39)$$

$$\frac{\partial u}{\partial C_i} = x_1 \frac{\partial u_1}{\partial C_i} + x_2 \frac{\partial u_2}{\partial C_i}$$

It is only the $-P \delta_{12} y_j^2$ term in expression for u which is a function of the constants C_i .

From the expression for u_1 , u_2 and equations (38e and (38f)

$$\frac{\partial u_2}{\partial C_i} = \frac{2P\delta_{12}}{RT} y_1^2 y_2 \frac{\partial \ln \alpha_{21}}{\partial C_i} \quad (40a)$$

$$\frac{\partial u_1}{\partial C_i} = -\frac{2P\delta_{12}}{RT} y_1 y_2^2 \frac{\partial \ln \alpha_{21}}{\partial C_i} \quad (40b)$$

From equation (24)

$$\frac{\partial \ln \alpha_{21}}{\partial C_i} = \frac{\partial u_2}{\partial C_i} - \frac{\partial u_1}{\partial C_i} + \frac{1}{RT} \frac{\partial}{\partial C_i} \left(\frac{\partial g^E}{\partial x_2} \right) \quad (40c)$$

The last term on the right handside in the above equation is determined from equation (27).

Equation (40a), (40b) and (40c) are solved simultaneously to get explicit relations for $\frac{\partial u_2}{\partial C_i}$, $\frac{\partial u_1}{\partial C_i}$ and $\frac{\partial \ln \alpha_{21}}{\partial C_i}$

$$\frac{\partial \ln \alpha_{21}}{\partial C_i} = \frac{\frac{\partial}{\partial C_i} \left(\frac{\partial g^E}{\partial x_2} \right)}{RT - 2P\delta_{12} y_1 y_2} \quad (40d)$$

$\frac{\partial g^E}{\partial C_i}$ can easily be obtained from equation (24) for all i from 1 to M.

The expression for $\frac{\partial w}{\partial C_i}$ will be similar to $\frac{\partial w}{\partial T}$ as given by equation (38j) except that instead of $\frac{\partial \ln \alpha_{21}}{\partial T}$, $\frac{\partial \ln \alpha_{21}}{\partial C_i}$ will be used.

With the help of equations (37) to (40) we can now determine the first derivatives of temperature with respect to elements C_i in \bar{C} . Returning back to equation (33)

$$\Delta T = \sum \frac{\partial T}{\partial C_i} \delta C_i \quad (33)$$

We determine the changes δC_i in C_i which will most nearly reduce the temperature residuals to zero. Least square technique is applied, that is we solve the equations

$$\begin{aligned}
 & \delta C_1 \sum \left(\frac{\partial T}{\partial C_1} \right)^2 + \delta C_2 \sum \frac{\partial T}{\partial C_1} \frac{\partial T}{\partial C_2} + \dots \delta C_M \sum \frac{\partial T}{\partial C_1} \cdot \frac{\partial T}{\partial C_M} \\
 & \quad = \sum \Delta T \frac{\partial T}{\partial C_1} \\
 & \delta C_1 \sum \frac{\partial T}{\partial C_1} \frac{\partial T}{\partial C_2} + \delta C_2 \sum \left(\frac{\partial T}{\partial C_2} \right)^2 + \dots \delta C_M \sum \frac{\partial T}{\partial C_2} \frac{\partial T}{\partial C_M} \\
 & \quad = \sum \Delta T \frac{\partial T}{\partial C_2} \\
 & \quad \vdots \\
 & \delta C_1 \sum \frac{\partial T}{\partial C_1} \frac{\partial T}{\partial C_M} + \delta C_2 \sum \frac{\partial T}{\partial C_2} \frac{\partial T}{\partial C_M} + \dots \delta C_M \sum \left(\frac{\partial T}{\partial C_M} \right)^2 \\
 & \quad = \sum \Delta T \frac{\partial T}{\partial C_M} \tag{41}
 \end{aligned}$$

A simultaneous solution of the above set of equations (41) yields δC_i . Adding these increments to the initial values of constants C_i we find improved approximations. Since the second derivatives of T with respect to C_i are not zero, these are not necessarily the best values, and it may be necessary to repeat the process until C_i do not change significantly. This procedure has not utilized the (y-x) experimental data, (y-x) relation can be predicted for the isobaric (T-x) data under consideration.

The above process essentially gives us the constants A, B, etc. in the Redlich-Kister expression for g^E , as functions of temperature. From the values of C_1 to C_M the constants A, B can be reconstituted at different temperatures. g^E is then obtained as a function of liquid composition alone. One can then

CHAPTER 7

DISCUSSION OF THEORETICAL RESULTS

In order to evaluate the method developed in last chapter (Theoretical Analysis) for the prediction of isothermal data from isobaric data, predicted results have been compared with available experimental data. The comparison has been done both in tabular form (Tables VII and VIII) as well as by plots (Figs. 11 to 27).

The systems chosen for comparison are non-polar + non-polar mixtures, non-polar + polar and polar + polar mixtures. These belong to the azeotropic as well as azeotropic groupings.

As a measure of deviation between experimental isothermal data and predicted isothermal data two quantities have been defined.

(i) Std_p, the standard deviation in total pressure

$$\text{Std}_p = \frac{\sum_{i=1}^n (P_{\text{calc}} - P_{\text{exptl}})^2}{n-1}$$

and

(ii) Std_y, the standard deviation in vapour phase composition

$$\text{Std}_y = \frac{\sum_{i=1}^n (y_{\text{calc}} - y_{\text{exptl}})^2}{n-1}$$

where n is the number of data points.

The extent of non-ideality of the system is given by the numerical

TABLE VII

PREDICTED ISOTHERMAL DATA AT A GLANCE

System	Temp. in °K	Std. dev. in P in mm Hg.	Std.dev. in y in mole fraction	Numerical value of A in Cal/g.mole	Form of the constant
I. $\text{CCl}_4(1)+\text{Cyclohexane}(2)$ (non-polar+non-polar) $\mathcal{E}(1)=2.238, \mathcal{E}(2)=2.220$ $P = 760 \text{ mm.}^{30}$	283^{26} 313^{28} 333^{27} 343^{29}	1.74 2.06 3.69 4.98 1.17	.0067 .0032 .0039 .0032 .0007	78.83 78.83 78.83 78.83 55.13	Independent of temperature " " " " $A=-958.3+2.95T$
II. $\text{CCl}_4+\text{C}_6\text{H}_6$ (non-polar+non-polar) $\mathcal{E}(1)=2.238, \mathcal{E}(2)=2.284$ $P = 760 \text{ mm.}^{31}$ (Fig. 11 and 12)	313^{32} 343^{32}	.51 .96	.0027 .0017	65.51 65.51	Independent of Temperature "
III. Benzene+Heptane (nonpolar+nonpolar) $\mathcal{E}(1)=2.284, \mathcal{E}(2)=$ $P = 760^{34}$	353^{33}	5.97	.0057	249.16	"
IV. $\text{CHCl}_3 + \text{C}_6\text{H}_6$ (nonpolar+nonpolar) $\mathcal{E}(1)=4.806, \mathcal{E}(2)=2.284$ $P = 760 \text{ mm}^{35}$	298^{36}	14.65	.0359	-371.78	"
V. Acetone+Benzene $\mathcal{E}(1)=20.7, \mathcal{E}(2)=2.284$ $P = 760^{38}$ (Fig. 14)	318^{37}	9.72	.0114	189.5	$A=1309.37-3.5T$

(Table VII continued)

VI. $\text{CCl}_4 + \text{Acetone}$ $\mathcal{E}(1)=2.238, \mathcal{E}(2)=20.7$ $P = 760 \text{ mm}^{39}$ (Fig. 13)	318 ⁴⁰	6.22	.0147	495.71	$A = -3402.46 + 20.27T$ $-.025 T^2$
VII. Ethylacetate + Propanol $\mathcal{E}(1)=6.02, \mathcal{E}(2)=20.1$ $P = 760 \text{ mm}^{41}$ (Figs. 20 & 21)	313 ⁴¹	3.40	.0215	607.17	$A = -2093.56 - 4.75T$
	333 ⁴¹	6.59	.0134	512.23	$A = -2093.56 - 4.75T$
VIII. Ethyl Ether + Ethanol $\mathcal{E}(1)=4.335, \mathcal{E}(2)=24.30$ $P = 760 \text{ mm}^{42}$ (Figs. 17, 18 & 19)	273 ⁴³	5.30	.0134	709.73	$A = 903.48 - 1.65T$ $+ .0035 T^2$
	283 ⁴³	8.18	.0151	712.42	"
	293 ⁴³	10.72	.0125	715.81	"
	298 ⁴⁴	9.40	.0176	717.76	"
	303 ⁴³	15.89	.0135	719.88	"
	313 ⁴³	19.22	.0142	724.64	"
IX. Acetone + Ethanol $\mathcal{E}(1)=20.7, \mathcal{E}(2)=24.30$ $P = 760 \text{ mm}^{45}$ (Figs. 15 & 16)	305 ⁴⁶	2.13	.0130	511.00	$A = 1089.74 - 1.90T$
	313 ⁴⁶	1.66	.0066	437.66	Independent of Temp.
		5.43	.0109	495.82	$A = 1089.74 - 1.90T$
	321 ⁴⁶	.90	.0055	437.66	Independent of Temp.
		6.89	.0113	480.65	$A = 1089.74 - 1.90T$
<u>Azeotropes</u>					
X. $\text{C}_6\text{H}_6 + n\text{C}_6\text{H}_{12}$ $\mathcal{E}(1)=2.284, \mathcal{E}(2)=2.220$ $P = 760 \text{ mm}^{48}$ (Figs. 11 & 22)	313 ⁴⁷	.90	.0022	272.60	Independent of Temp.
	343 ⁴⁷	1.68	.0028	272.60	"

(Table VII continued)

XI. Methanol-Ethylacetate $\epsilon(1)=32.63$, $\epsilon(2)=6.02$ P = 760 mm ⁴⁹ (Figs. 23,24 & 25)	313 ⁵⁰	6.56	.0167	679.70	643.29+.12T
	323 ⁵⁰	3.06	.01222	664.70	Independent of Temperature
	333 ⁵⁰ ₁	7.73	.0132	A=663.92 B=-14.90	Two constants Independent of Temperature
XII. Ethanol-Benzene $\epsilon(1)=24.30$, $\epsilon(2)=2.284$ P = 750 mm ⁵³ (Figs. 26 & 27)	313 ⁵¹	9.37	.0357	1094.45	A=1885.32 - 2.53T
	328 ⁵²	11.93	.0395	1204.82	A=12562.97 - 59.06T+.074T ²
	333 ⁵¹	17.65	.0348	1099.87	"

$\epsilon(1)$, $\epsilon(2)$ are the dielectric constants of the components.

TABLE VIII

COMPARATIVE STUDY OF STANDARD DEVIATION IN PRESSURE

System	Standard deviation in pressure with			
	Single constant	Linear temp. dependence of Δ	Quadratic temp.dep. of Δ	Two constants temperature independent
$\text{CHCl}_3 + \text{C}_6\text{H}_6$ (298°K) (nonpolar+ nonplar)	14.64	45.65	48.43	21.83
$\text{CCl}_4 + \text{Acetone}$ (318°K) (nonpolar + polar)	12.17	12.02	6.22	11.69
Ethylacetate + Propanol (313°K) (nonpolar + polar)	8.17	3.40	20.99	7.18
Acetone+Ethanol (305°K) (polar + polar)	5.33	2.13	7.07	-
$\text{C}_6\text{H}_6 + \text{Cyclohexane}$ (313°K) (nonpolar+nonpolar azeotrope)	.90	9.05	9.29	4.25
$\text{C}_2\text{H}_5\text{OH} + \text{C}_6\text{H}_6$ (328°K) (Polar+non-polar azeotrope)	30.76	18.42	11.93	26.19

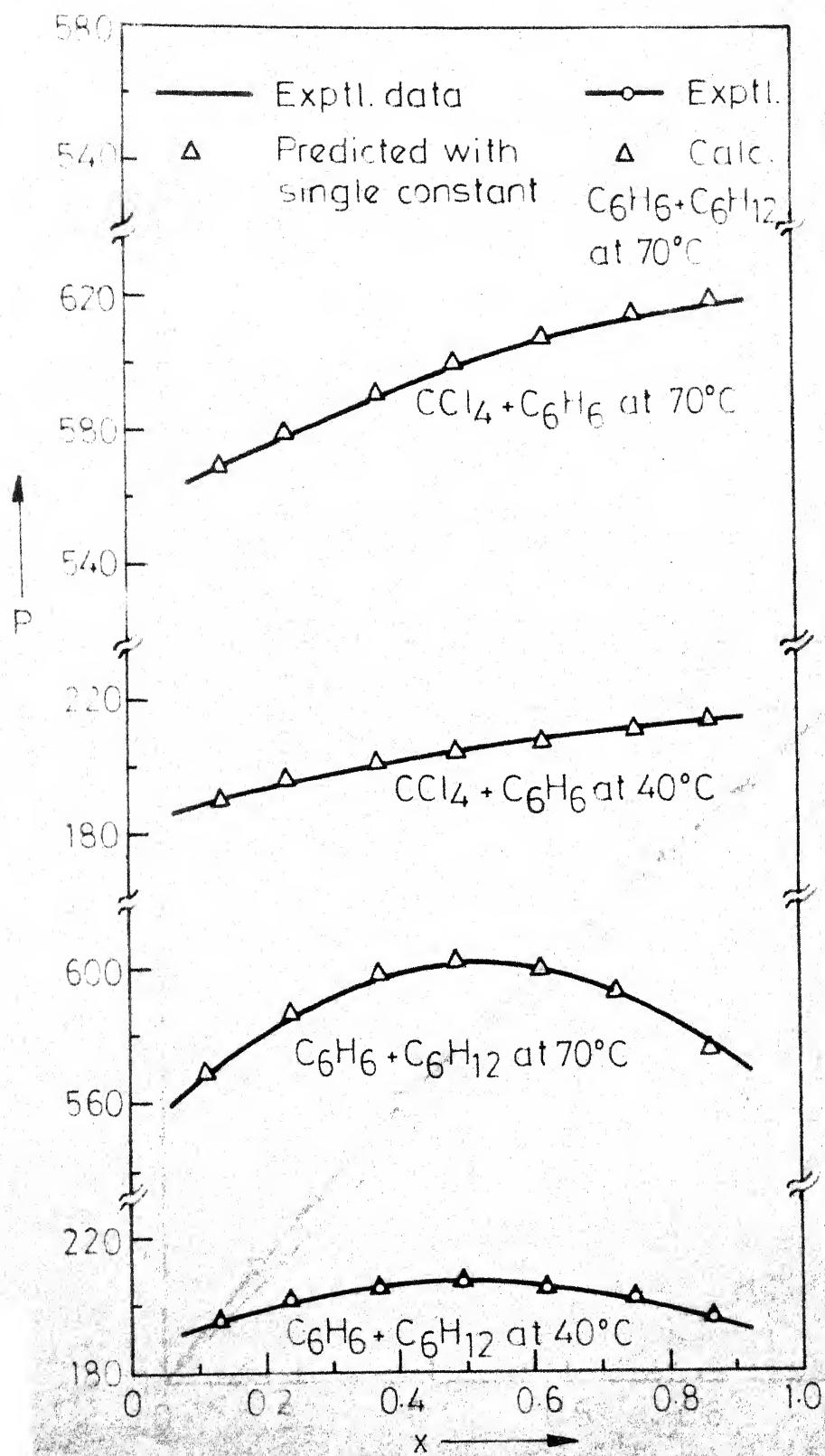


Fig11-Vapor pressure vs. liquid composition.

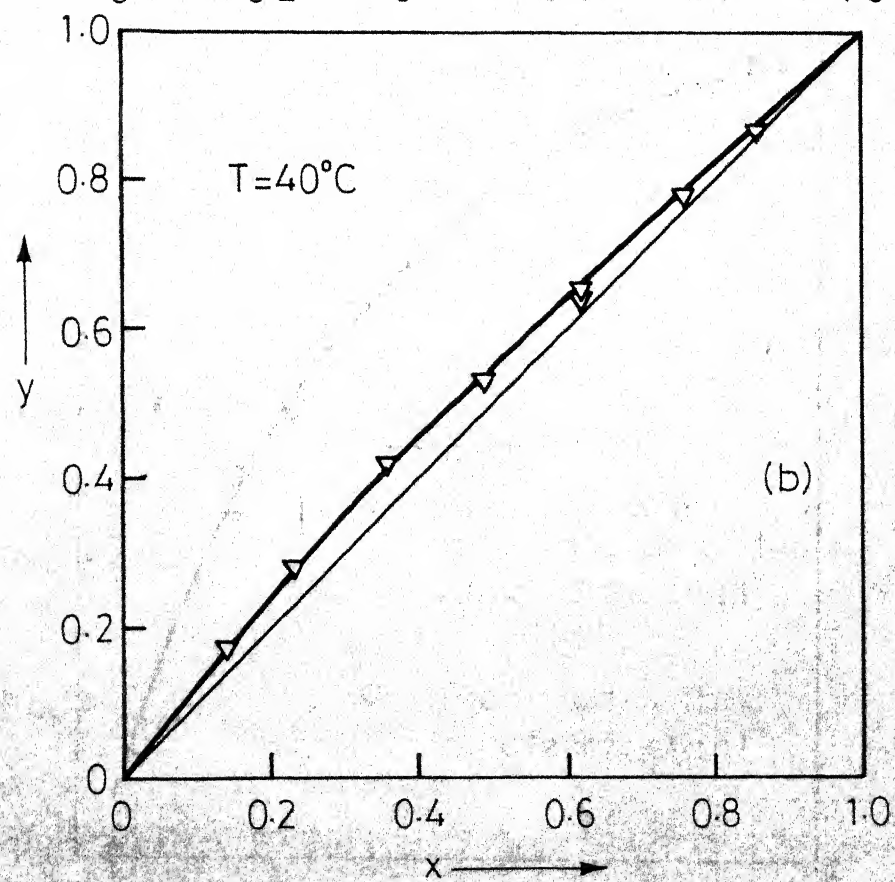
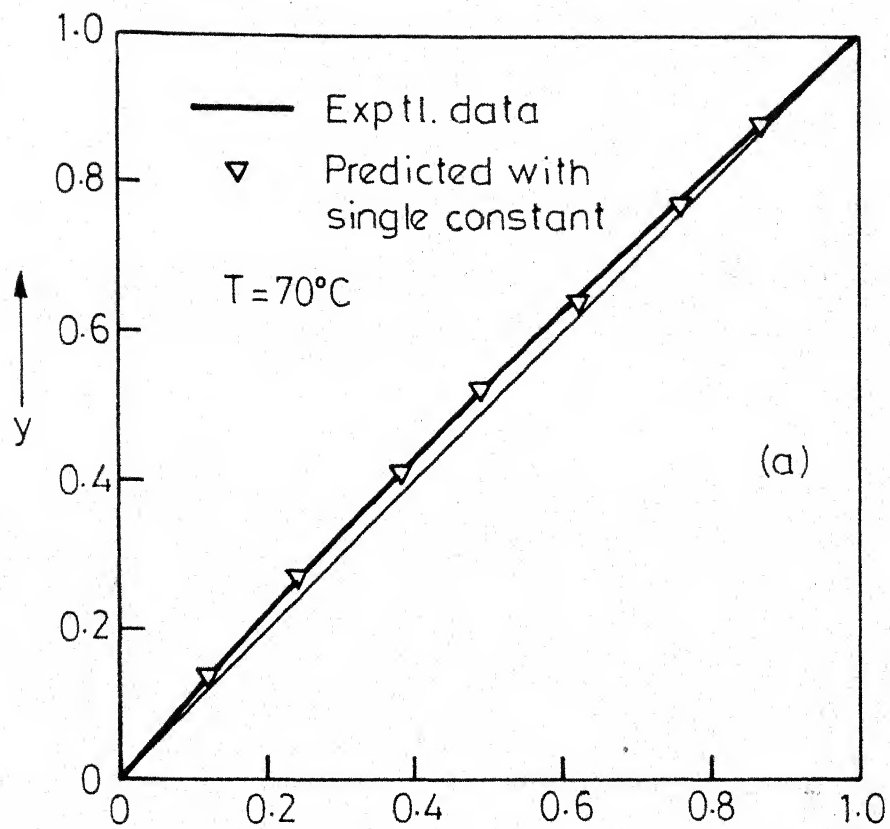


Fig. 12 - Vapor composition vs. liquid composition for Carbon Tetrachloride + Benzene.

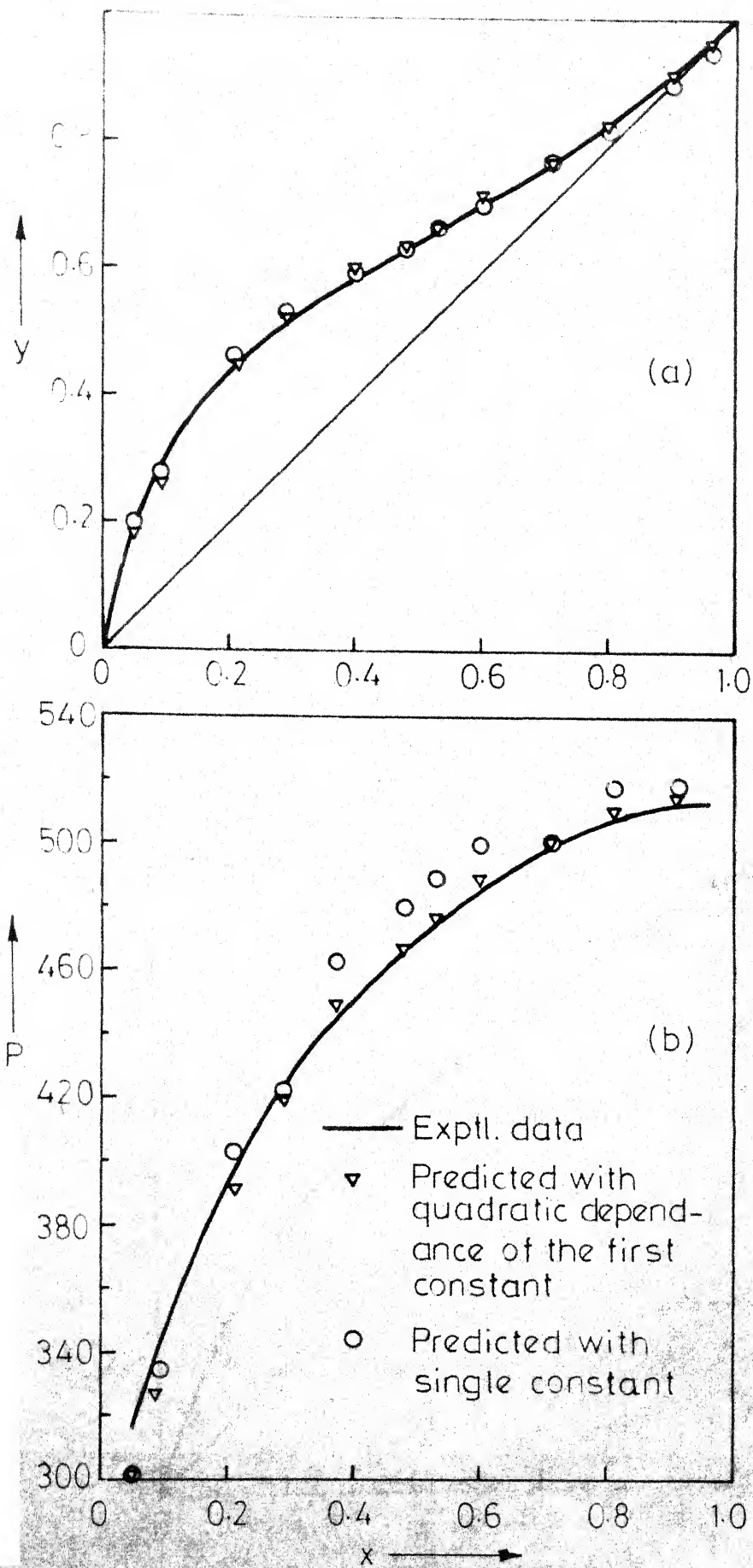


Fig.13- Equilibrium data for carbon Tetrachloride-Acetone at 40°C.

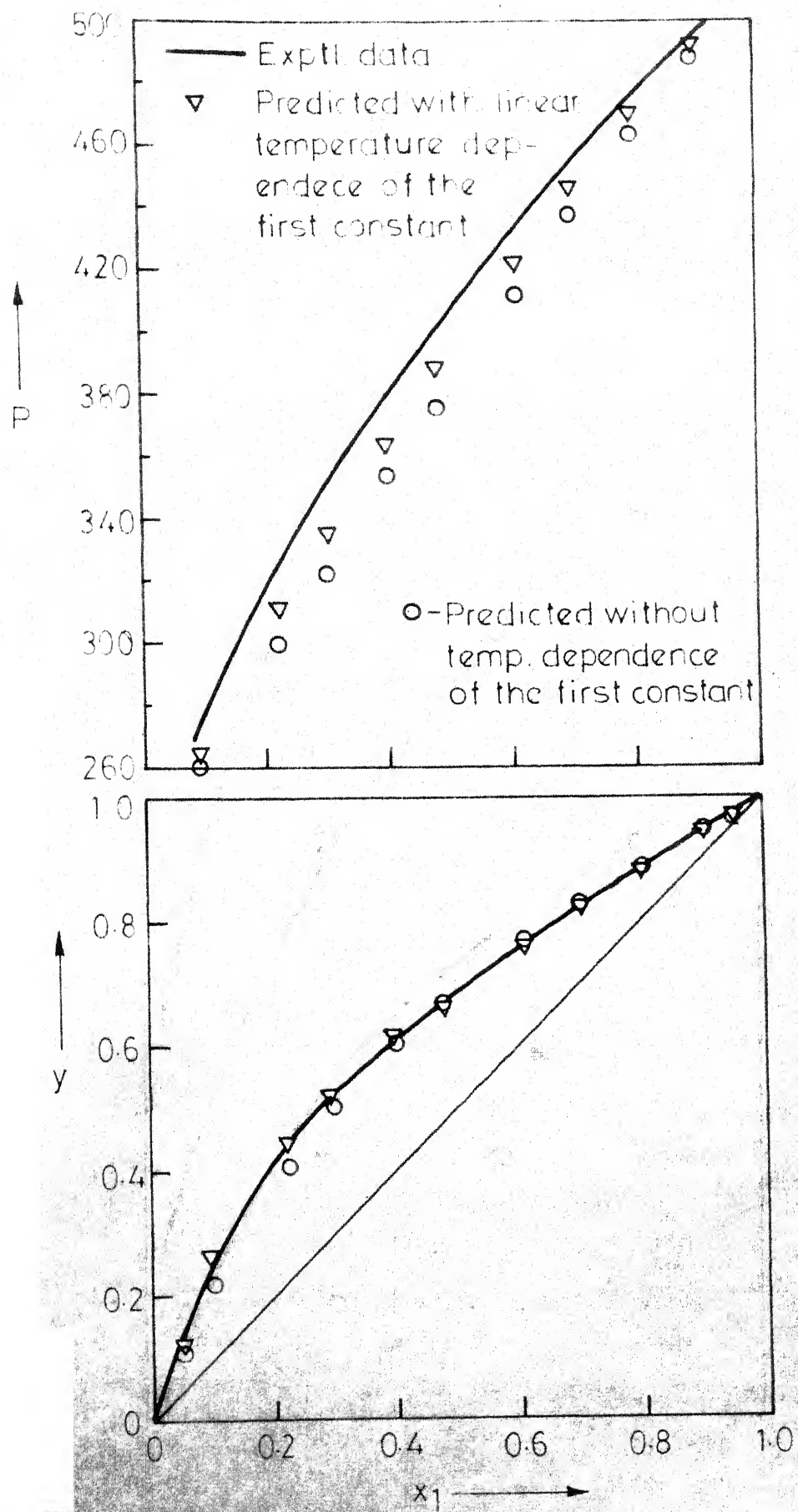


Fig. 14 - Equilibrium data for Acetone(1) - Benzene(2).

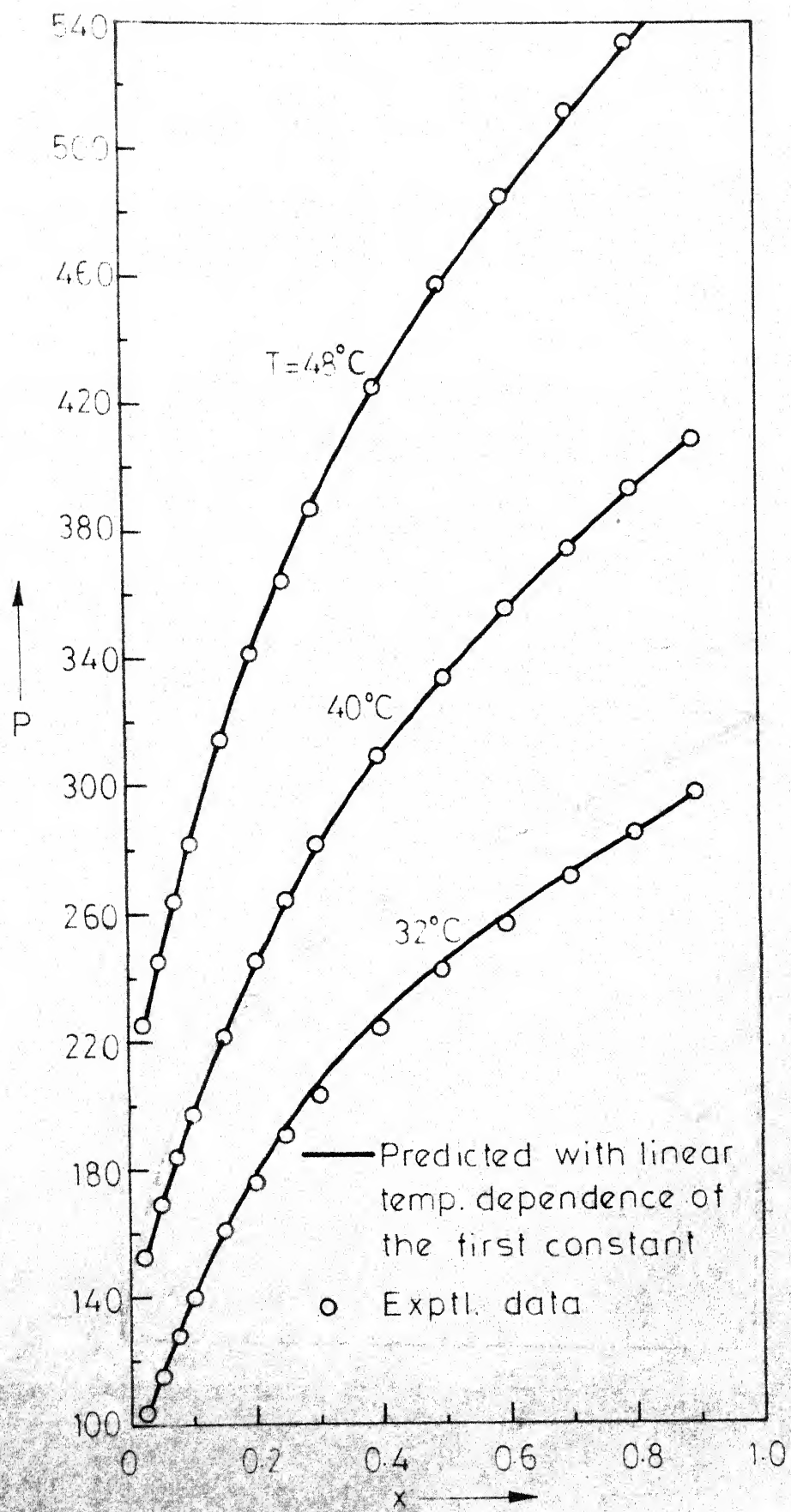


Fig.15 - Vapor pressure vs. liquid composition for Acetone - Ethanol.

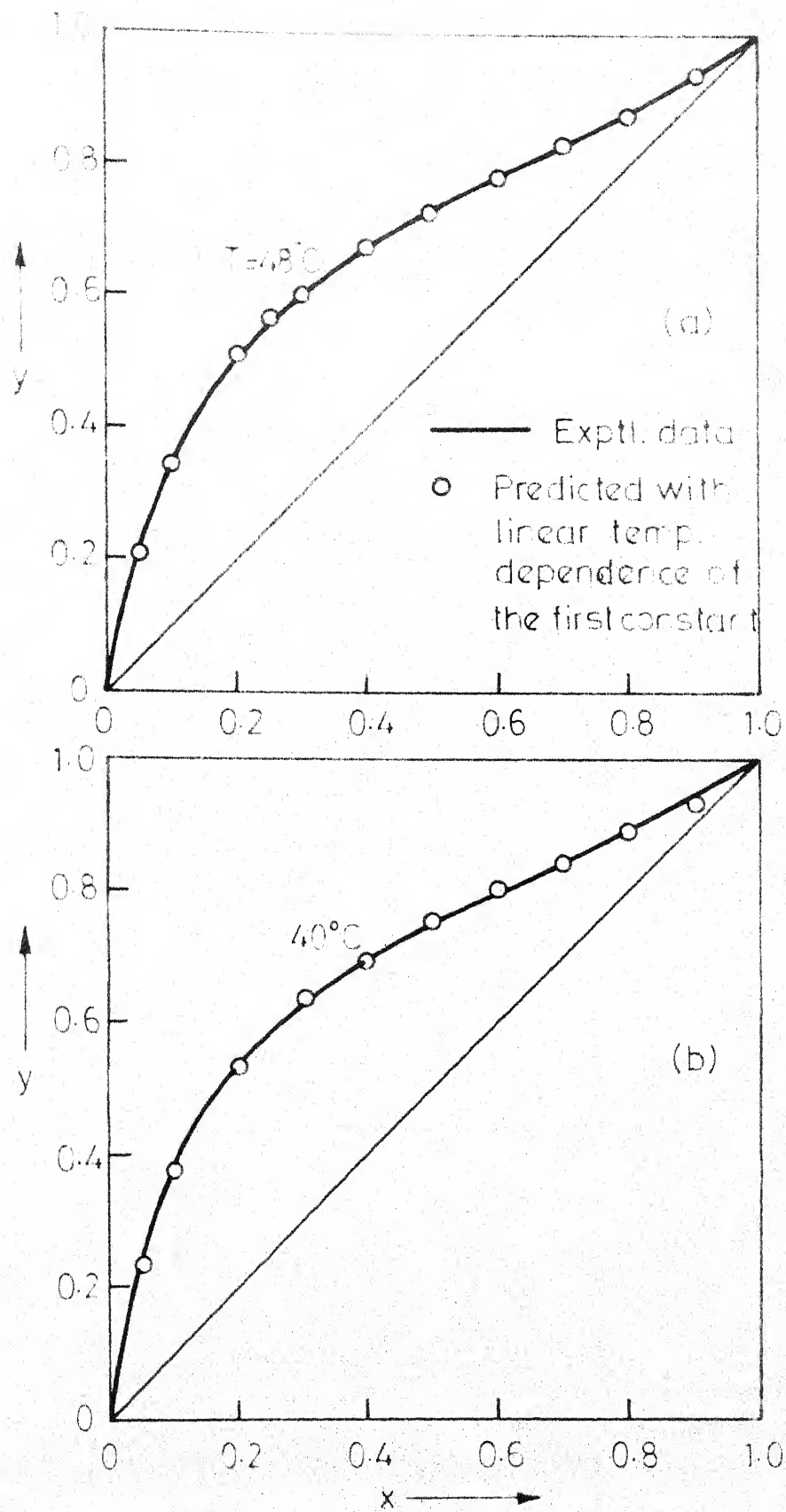


Fig.16 - Vapor composition vs. liquid composition for Acetone - Ethanol.

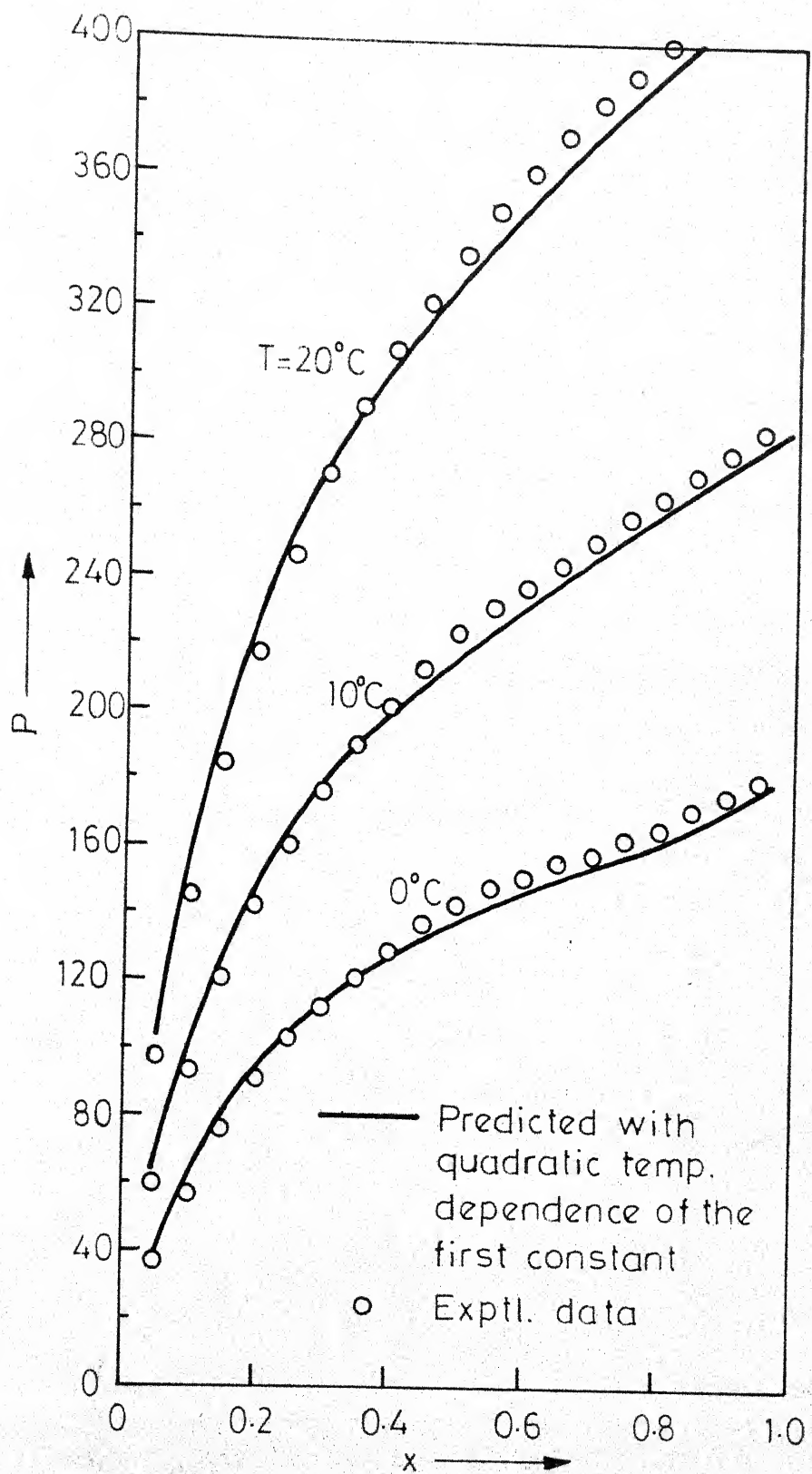


Fig.17 - Vapor pressure vs. liquid composition for Ethyl Ether-Ethanol.

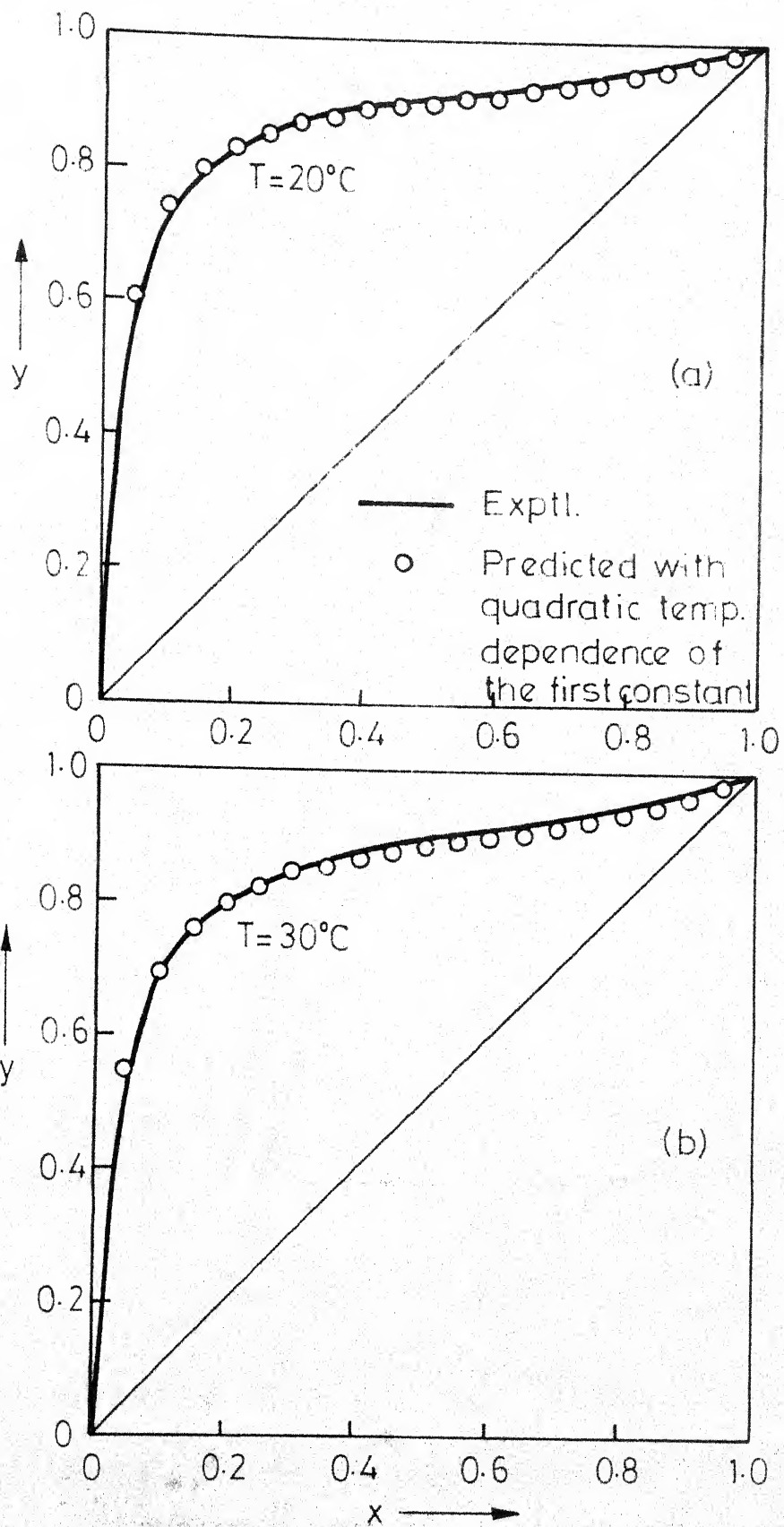


Fig.18 - Vapor composition vs. liquid composition for Ethyl Ether - Ethanol.

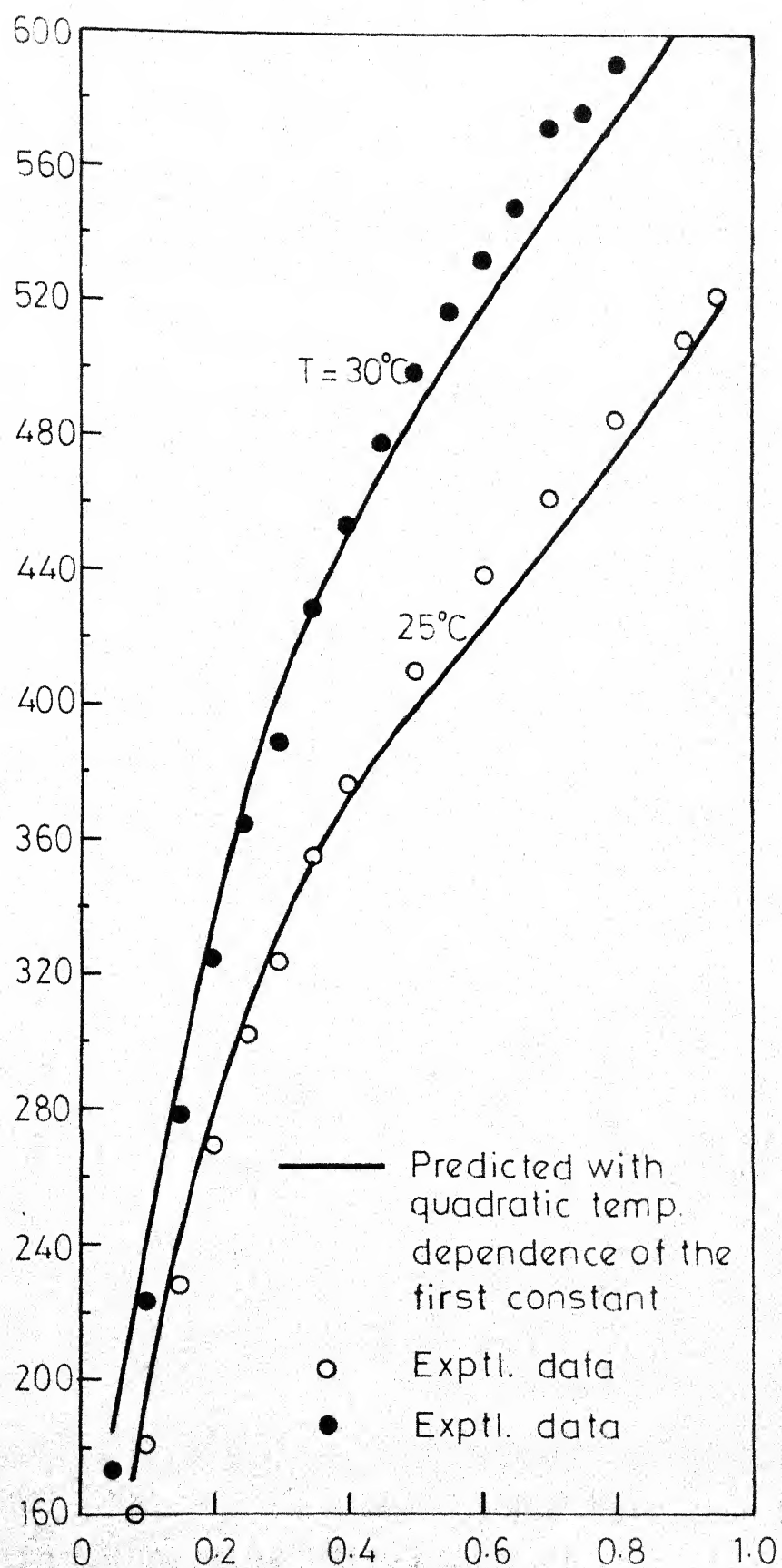


Fig.19 - Vapor-pressure vs. liquid composition for Ethyl Ether-Ethanol.

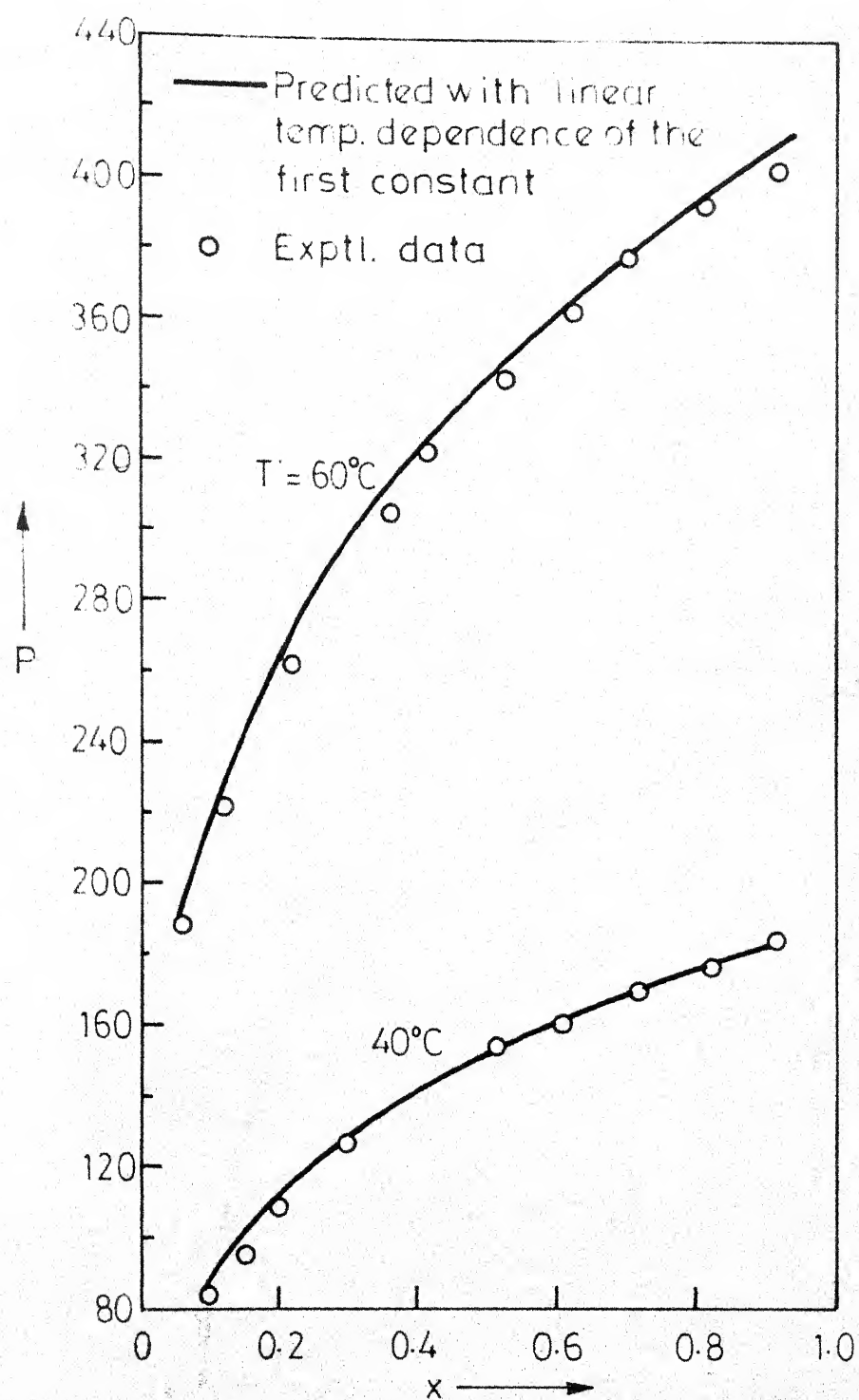


Fig.20 - Vapor-pressure vs. liquid composition for Ethyl Acetate-Propanol.

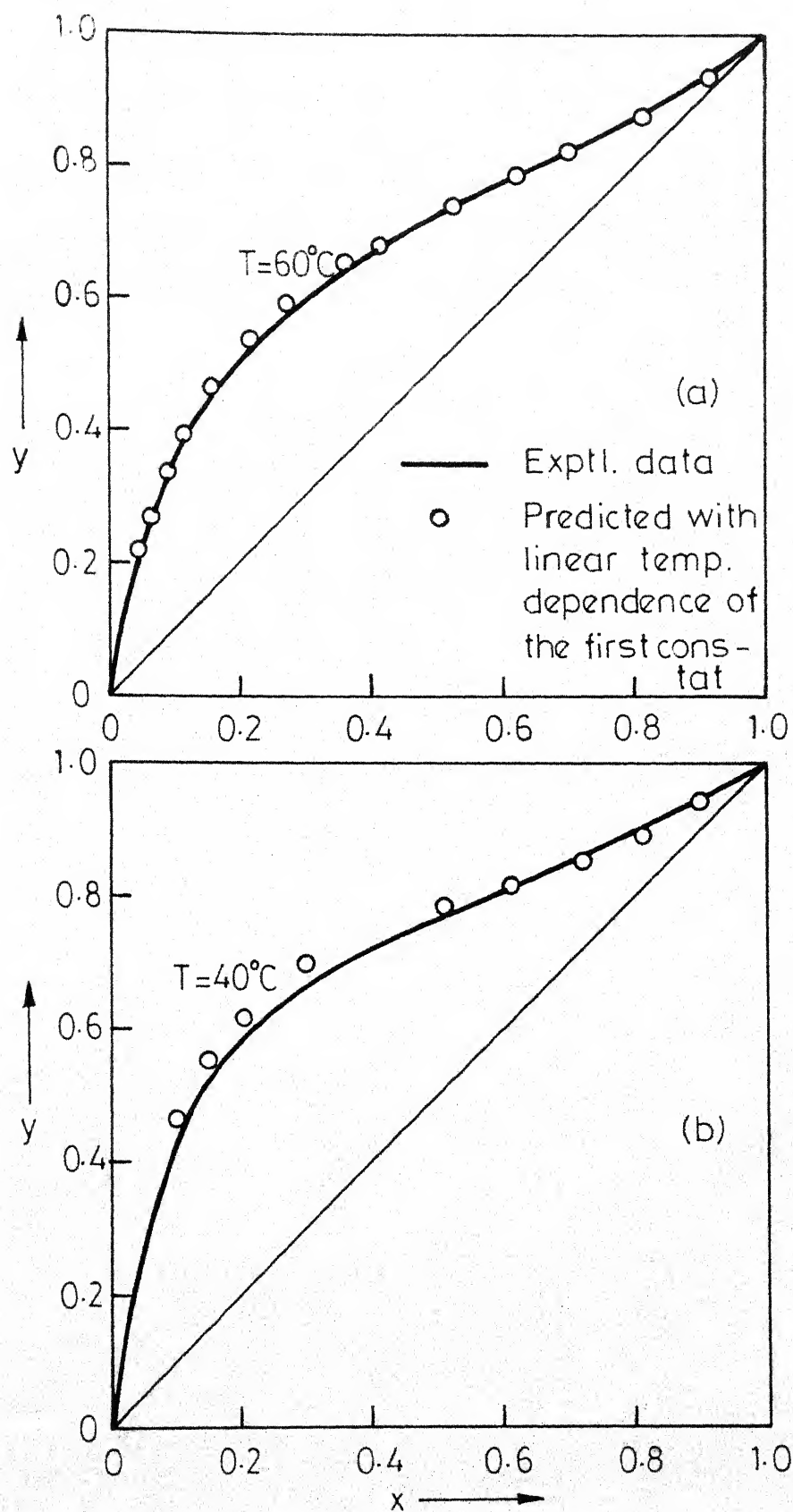


Fig.21 - Vapor-composition vs. liquid composition for Ethyl Acetate - Propanol.

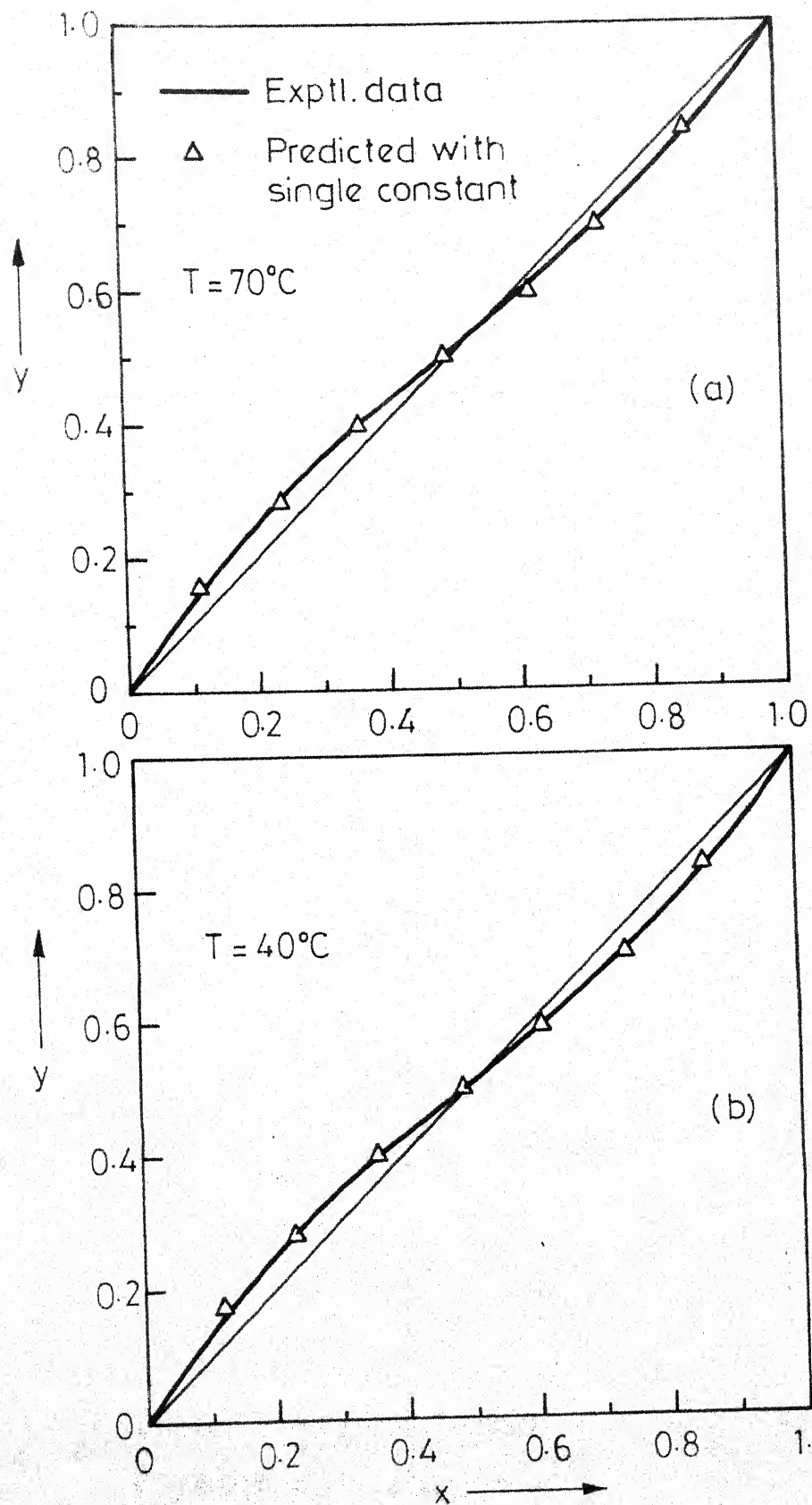


Fig 22 - Vapor composition vs. liquid composition for Benzene + Cyclohexane.

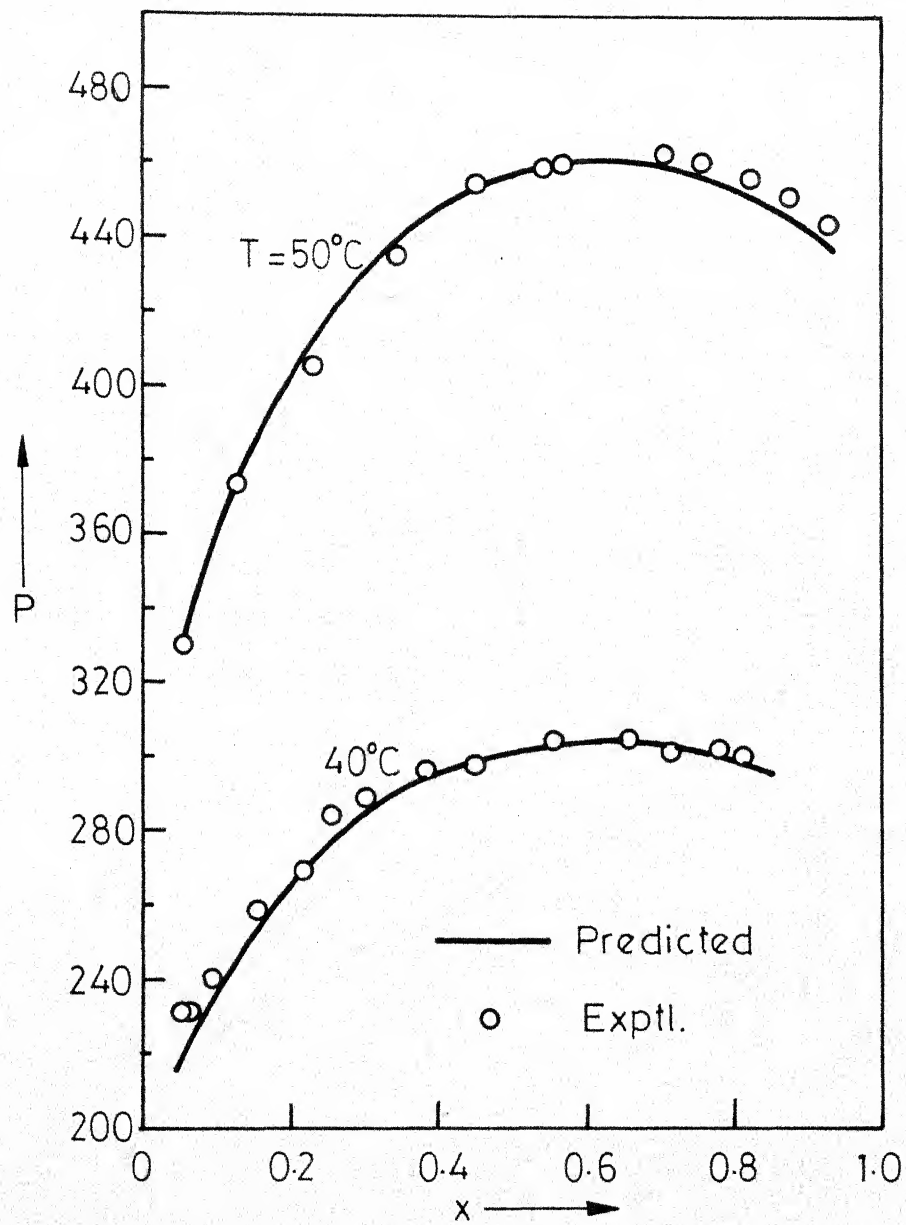


Fig.23 - Vapor pressure vs. liquid composition for Methanol-Ethyl Acetate.

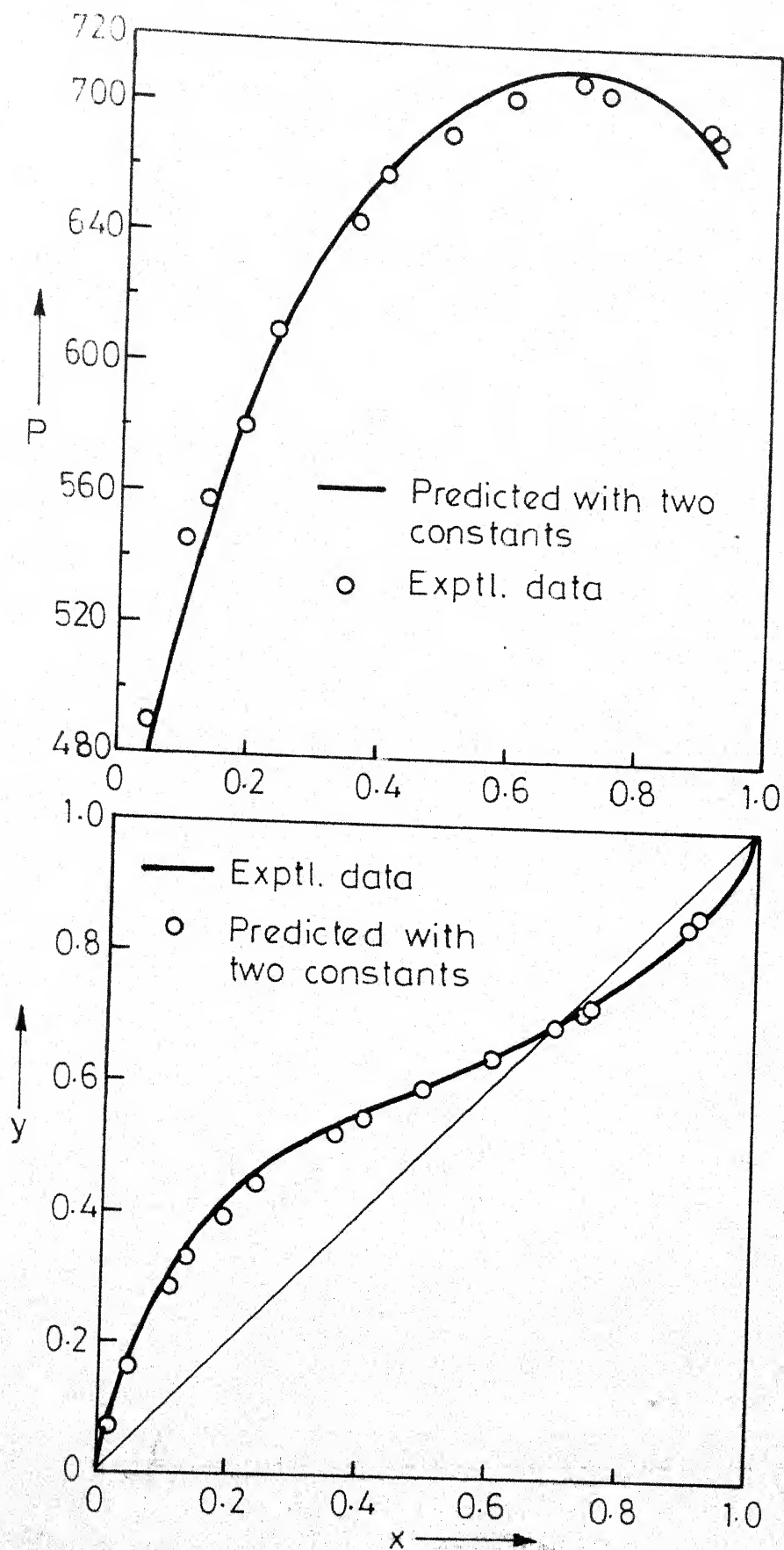


Fig.24- Equilibrium curves for Methanol-Ethyl Acetate at 60°C.

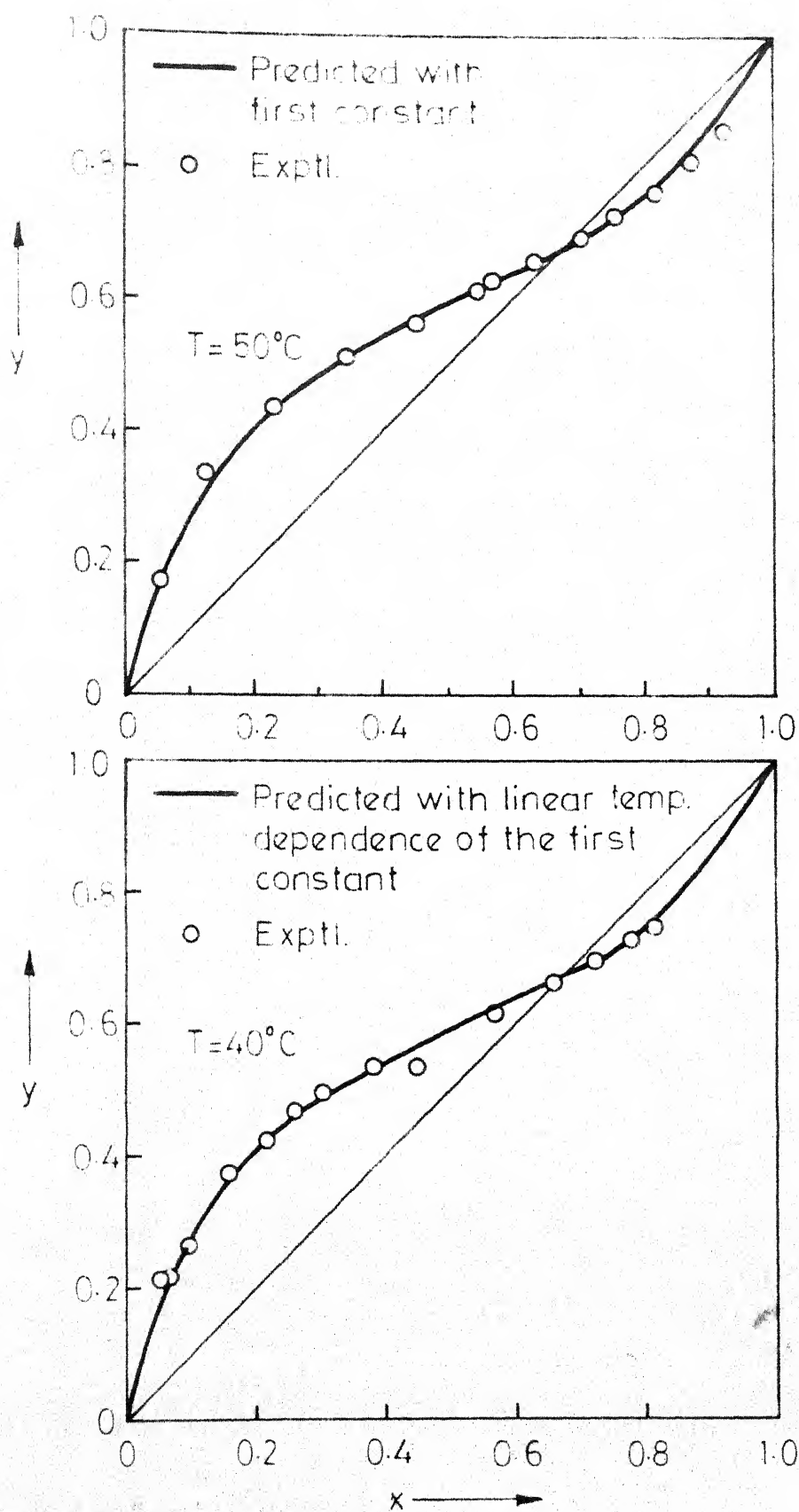


Fig. 25- Vapor composition vs liquid composition for Methanol-Ethyl Acetate.

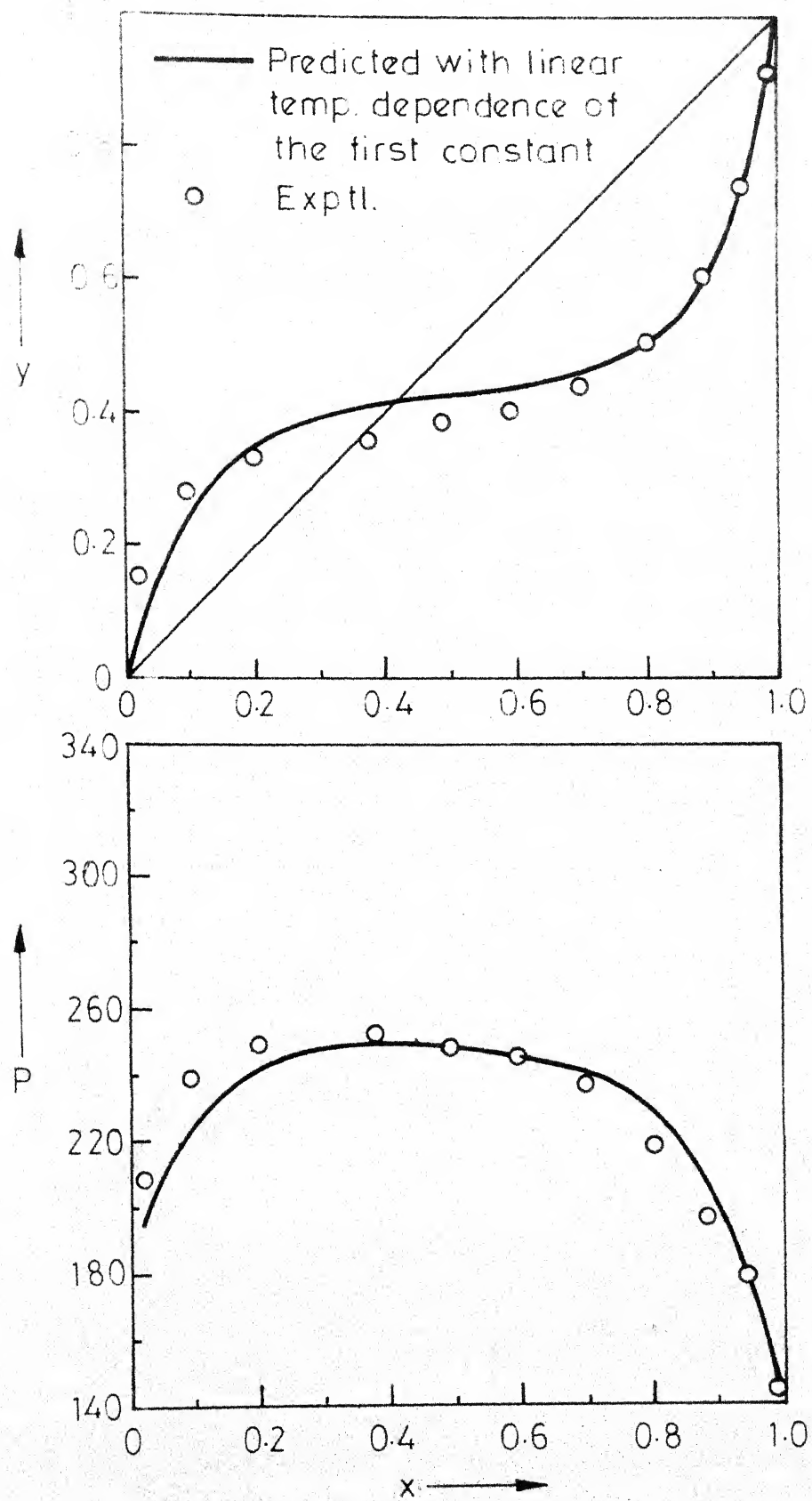


Fig.26-Equilibrium curves for Ethanol-Benzene at 40°C.

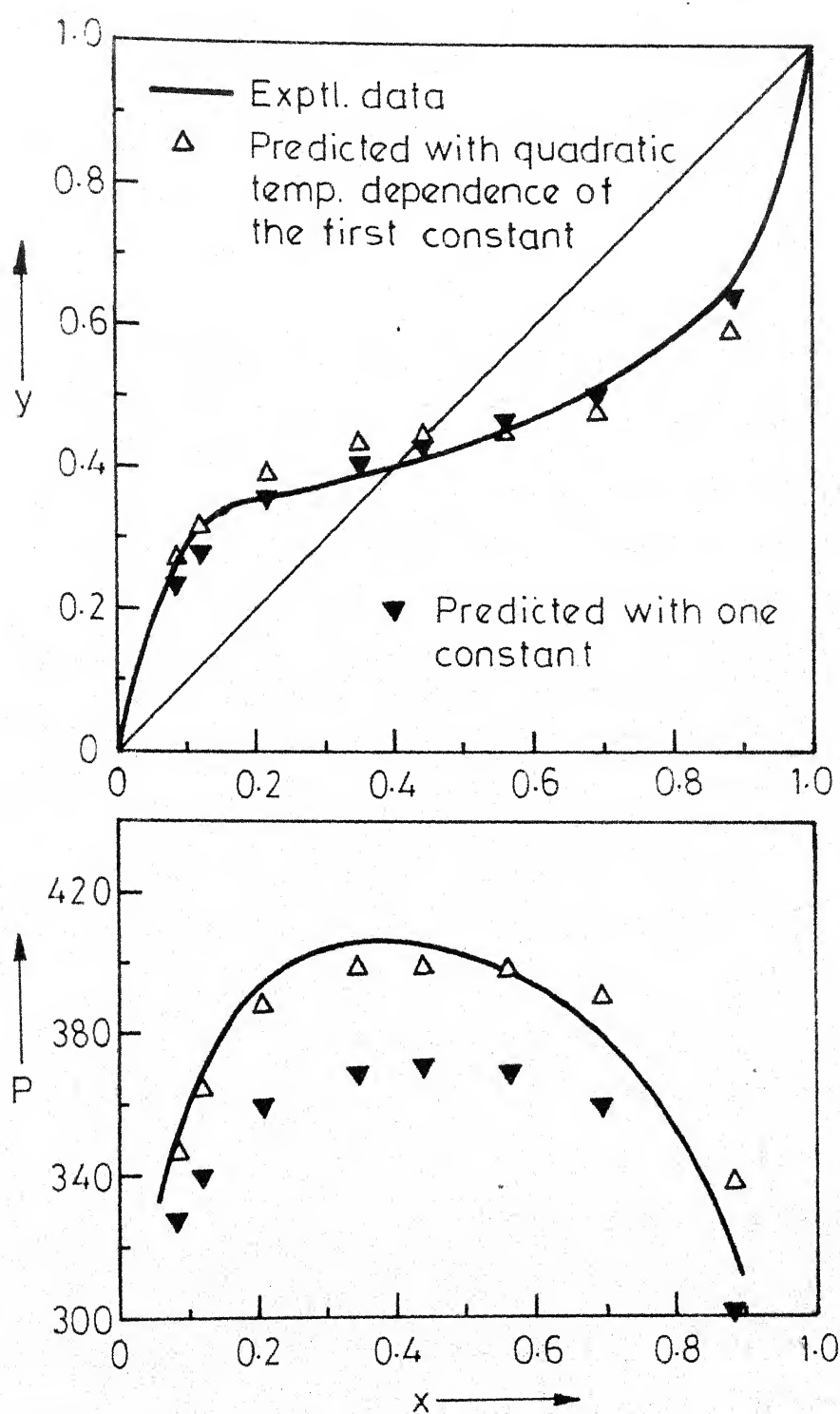


Fig.27- Equilibrium data for Ethanol-Benzene at 55°C.

value of the constant A. The extent of polarity of the compound is gauged by the value of the dielectric constant.

Before discussing the obtained results a basic contradiction in the analysis will be outlined. In order to accommodate the assymetry in isothermal g^E one must have more than one constant in the Redlich-Kister expression for g^E , and in order to include the concept of irregular solutions ($S^E \neq 0$) these constants must be made temperature dependent. That is when isobaric data is analyzed one calculates more number of constants (C_i) than are apparently needed for isothermal data (A,B,C etc.). The increase in number of constants (C_i) will reduce the number of degrees of freedom and thereby lessen the chance of improving the values of the constants C_i by successive iterations in the least square analysis. Therefore most of the results have been obtained with one constant A (implying regular solution) but with temperature dependence (i.e. not strictly regular).

Looking at Table VII it is found that for non-polar +non-polar mixtures the behaviour is strictly regular- the constant A has no temperature dependence. The value of A evaluated from experimental isobaric data is valid over all temperatures. The predictions agree well for systems $\text{CCl}_4 + \text{Cyclohexane(I)}$, $\text{CCl}_4 + \text{C}_6\text{H}_6(\text{II})$, Benzene + Heptane(III), and Chloroform + Benzene (IV). For systems (I), (II), (III) the standard deviations in pressure are less than 5 mm, and standard deviation in vapour composition less than 1%. That (IV) has much larger deviations in pressure

and vapour composition can be due to its higher non-ideality ($A = -371.78$), slightly polar nature of chloroform. However from Table VIII it is seen that results for (IV) are best with one constant only, two constants (A,B) giving higher deviation in P. That there is a slight anomaly in CCl_4 + cyclohexane at $T = 343^\circ\text{K}$ - better results are obtained with linear dependence on temperature of A, indicates that non-polar + non-polar systems can be slightly irregular.

For the non-polar + polar systems - Acetone + Benzene (V), CCl_4 + Acetone (VI), Ethylacetate + Propanol (VII) and Ethyl Ether + Ethanol (VIII), we observe from Table VII that (i) nonideality is more (A is higher than in non-polar + non-polar mixtures), (ii) there is a clear dependence on temperature indicating the irregularity of the system, (iii) the standard deviations in P and y based on single constant A are more than for non-polar + non-polar systems indicating that there exists more asymmetry in isothermal g^E , however (iv) irregularity of the system is a more important consideration than the asymmetry in isothermal g^E , for Table VIII indicates that for systems CCl_4 + Acetone and Ethyl Acetate + Propanol stdp is less for a single temperature dependent constant than for two temperature independent constants. The changes occurring in A values for $\Delta T = 10^\circ\text{K}$ at $T = 300^\circ\text{K}$ are 13%, 14%, 7% and .6% for systems V, VI, VII and VIII. That larger deviations are obtained for ethylether and ethanol with temperature dependent constant, and there is negligible change in value of A with temperature indicates that perhaps for this system irregularity

concept is not that important, one could do better with higher constants temperature independent in Redlich-Kister expression. In all these predictions one thing should be noted that these isotherms do not intersect the isobaric data, that is these predictions are essentially extrapolations.

For the polar + polar system Acetone + Ethanol the value of A is temperature dependent but it appears that it is not linear, it might be exponentially decaying with temperature. Again in this case the predictions are essentially extrapolations.

For the azeotropes not many systems have been studied. For the close boiling, non-polar + non-polar mixture $C_6H_6 + C_6H_{12}$ the behaviour is regular, indicated by predictions with stdp < 2 mm and stdy $< .5\%$. Among the non-polar + polar systems - for methanol + ethyl acetate dependence on temperature is weak and one could do as well with two temperature independent constants; for ethanol benzene temperature dependent constant is better than just two constants, however the deviations in P and y are large indicating that two temperature dependent constants might have been better than either a single temperature dependent constant or two temperature independent constants.

In this discussion it must be remarked that all the mixtures studied have had a unimodal plot of $g^E(T, x)$ vs. x . But there are few systems which are not unimodal and have more than one peak - for example Acetone + BuOH²⁴ has one minima and two maxima and $CCl_4 + CH_3OH$ ²⁵ has two minima and one maxima. In such cases one

should have a higher degree of polynomial expression for g^E . For the systems Acetone + BuOH and $\text{CCl}_4 + \text{CH}_3\text{OH}$ it should be 4th order - having four constants A,B,C,D in Redlich-Kister expression.

For the system Methylcyclohexanol + Methylcyclohexane ($\text{C}_7\text{H}_{14}\text{O} + \text{C}_7\text{H}_{14}$) $\ln \gamma_1/\gamma_2$ has three peaks - two maxima and one minima, that is $\ln \gamma_1/\gamma_2$ is a 4th order polynomial in x. And since $\ln \gamma_1/\gamma_2 = 1/RT \times (\partial g^E/\partial x_1)$, g^E is necessarily fifth order. Hence, Malesinski's prediction with single constant will not suffice.

CONCLUSION:

From the above results it is concluded that

- (i) non-polar + non-polar mixtures behave as strictly regular solutions i.e. $S^E=0$, and therefore in $g^E = A x_1 x_2$, A can be used for all temperatures.
- (ii) non-polar + polar mixtures show a clear dependence on temperature of the constant A, indicating that the nature of association alters with temperature. Same is the case for polar + polar mixtures. However, the dependence on temperature need not be linear or quadratic, it can have other forms of dependence - say exponential.
- (iii) Isothermal data can be predicted even at those temperatures which do not lie in the range of isobaric T-x-y; that is extrapolations are possible.
- (iv) the shape of isobaric g^E gives a clue to the number of constants needed in the Redlich-Kister expression. For a g^E with n peaks, n constants are needed.

CHAPTER 8

RECOMMENDATIONS

For the system methylcyclohexanol + methylcyclohexane the thermodynamic consistency test remained invalid because of the absence of heat of mixing data. It is recommended that the heat of mixing data should be experimentally measured for the above system.

In all the isothermal predictions carried out (i) experimental isobaric data was used (ii) B_{12} , the interaction virial coefficient was assumed to be an arithmetic mean of pure component virial coefficients B_{11} and B_{22} (iii) single precision was used in Fortran IV on IBM 7044. It is recommended that the isobaric data should be smoothened and tested for thermodynamic consistency before employing for isothermal prediction, the interaction virial coefficient should be estimated from experimental data or predicted using a suitable model with realistic combining rules. Kreglewski's model can be utilized for calculation of B_{12} as a function of temperature, u_{12} being given as a harmonic mean of u_{11} and u_{22} and packing factor b calculated as a function of pseudo-critical temperature. Double precision should be used in order to match the sensitivity of the variables. Calculations should be performed with more number of degrees of freedom, i.e. more isobaric experimental data points. To get better isothermal predictions the isobaric plane should be selected such that extrapolation is avoided.

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REFERENCES

1. Othmer, D.F., Ind. Eng. Chem., 20, 745 (1928).
2. Jones, C.A., Schoenborn, E.M. and Colburn, A.P., Ind. Eng. Chem., 35, 666 (1943).
3. Gillespie, T.C., Ind. Eng. Chem. Analytical, 18, 575 (1946).
4. Landwehr, J.C., Yerazunis, S. and Steinhauser, H.H.,
5. Yerazunis, S., Plowright, J.D. and Smola, F.M., A.I.Ch.E., Jour., 660, September 1964.
6. Temperature its Measurement and Control in Science and Industry.
7. Haase, R, Z. Elektrochem, 35, 29 (1951).
8. Advances in Chemistry Series, Physical Properties of Chemical Compounds, Vol. 22.
9. Myers, H.S., Ind. Eng. Chem., 48, 1104 (1956).
10. Kreglewski, A., J. Phys. Chem., March 1969.
11. Yen and Woods, A.I.Ch.E.J., 12, No.1, 95 (1966).
12. Martin, J.J., "Thermo & Transport Properties of Gases, Liquid and Solids, Amer. Soc. Mech. Eng., N.Y., 1959, p. 110.
13. Sherwood and Reid, "Properties of Gases and Liquids, McGraw-Hill, N.Y., 1965.
14. Malensinski, W., Azeotropy and Other Theoretical Problems of Vapour Liquid Equilibrium, Interscience Publishers.
15. Swietoslowski - Ebulliometric Measurements.
16. Transaction American Inst. Chem. Engrs., 41, 371 (1945).
17. Journal of Chemical Society, 101, 1104 (1912).
18. Journal Chemical Engg. Data, 10, 106 (1965).
19. Journal Chemical Engg. Data, 10, 106 (1965).
20. Journal Chemical Engg. Data, 8(4), 549 (1963).
21. Transaction American Inst. Chem. Engrs., 41, 371 (1945).
22. Industrial Engg. Chemistry, 44, 2428 (1952).
23. Mukherjee, A., M.Tech. Thesis, IIT-Kanpur (1972).
24. Michalski, H., Michalowski S., Serwinski, M., Strumillo, C., ZESZYTY NAUK. POL. LOD7, NR, 36, 73 (1961).
25. Hipkin, H., Myers, H.S., Ind. Eng. Chem., 46, 2524 (1954).
26. Dvorak, K., Boublik, T., Collection Czech.Chem.Comm. 28, 1249(1963).
27. Dvorak K., Boublik, T., Collection Czech.Chem.Comm. 28, 1249 (1963).
28. Scatchard, G., Wood S.E., Mochel, J.M., J.Am.Chem.Soc., 61, 3206 (1939).
29. Brown, I., Ewald, A.H., Austr. J.Sci. Res. A3, 306 (1950).

30. Yuan, K.S., Lu, B.C.Y., J.Chem.Eng. Data 8(4), 549 (1963).
31. Fowler, R.T., Lim, S.C., J. Appl. Chem., 6, 74 (1956).
32. Fowler, R.T., Lim, S.C., J. Appl. Chem., 6, 74 (1956).
33. Brzostowski, W., Bull. Acad. Polon. Sci. Ser. Chim. 8, 291 (1960).
34. Brwn, I., Austr. J. Sci. Res. A5, 530 (1952).
35. Nagata, I., J.Chem.Eng. Data 7(3), 360 (1962).
36. Kireev, V.A., Sitnikov, I.P., Zh.Obshch. Khim. 16, 979 (1946).
37. Brown, I. Smith, F. Austr. J. Chem. 10, 423 (1957).
38. Reinders, W., De Minjer, C.H., Rec. Trav. Chim. Pays Bas 59, 309 (1940).
39. Acharya, M.V.R., Venkata Rao, C., Trans. Indian Inst. Chem. Engrs., 6, 129 (1953-1954).
40. Brown, I. Smith, F., Austr. J. Chem. 10, 423 (1957).
41. Murti, P.S., Van Winkle, M. Chem. Eng. Data Series 3, 72 (1958).
42. Kireev, V.A., Khachadurova, E.M., Zh. Prikl. Khim. 7, 495 (1934).
43. Nagai, J. Isii, N.: J.Soc. Chem. Ind. Japan 38, 8(1935).
44. Gordon, A.R., Hornibrook, E. J. Can.J.Res., 248, 263 (1946).
45. Duttey, Private Communication to T.H. Chilton, 1935. (Chu J.C.Et. Al., Distillation Equilibrium Data, 1950).
46. Gordon, A.R. Hines, W.G., Can.J. Res. 24B, 254 (1946).
47. Scatchard, G., Wood, S.E. Mochel, J.M., J. Phys.Chem., 43, 119 (1939).
48. Richards, A.R., Hargreaves, E., Ind.Eng.Chem., 36, 805 (1944).
49. Akita, K., Yushida, F., J.Chem.Eng.Data, 8(4), 484 (1963).
50. Murti, P.S., Van Winkle, M. Chem.Eng.Data Series 3, 72 (1958).
51. Udovenko, V.V., Fatkulina, L.G., Zh.Fiz. Khim., 26, 719 (1952).
52. Ho, J.C.K., Lu, H.C.Y., J.Chem.Eng. Data 8(4), 549 (1963).
53. Tyrer, D., J.Chem.Soc. 101, 1104 (1912).

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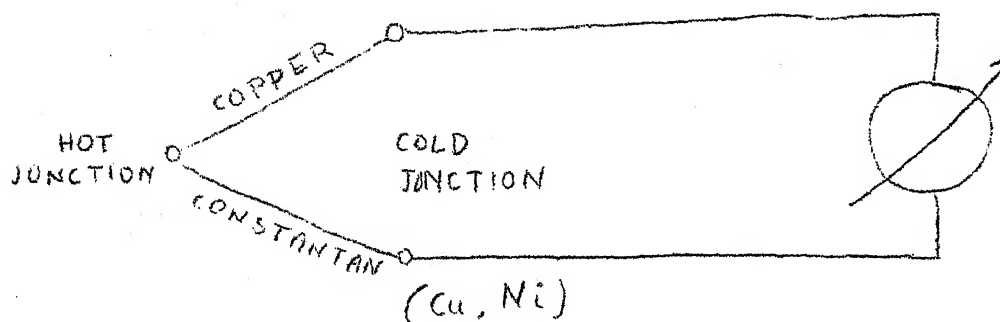
APPENDIX 1

DETAILS OF THERMOCOUPLE-CALIBRATION

".....I sought a method which above all would be rapid and simple, and decided on the use of thermo-electric couples..."

Henri Le Chatelier(1885)

Principle of Thermocouple



This is a very simple thermocouple circuit employed in the measurement of temperature. According to the laws of thermoelectricity small electromotive forces are generated in such a circuit. Briefly these laws amount to the following information.

- (1) If each section of wire in the circuit is homogeneous, that is if there is no change in composition or physical properties along its length, then the emf in the circuit depends only on the nature of the metals and the temperatures of the junctions.
- (2) If both of the junctions involving a particular homogeneous metal are at the same temperature, this metal makes no net contribution to the emf.

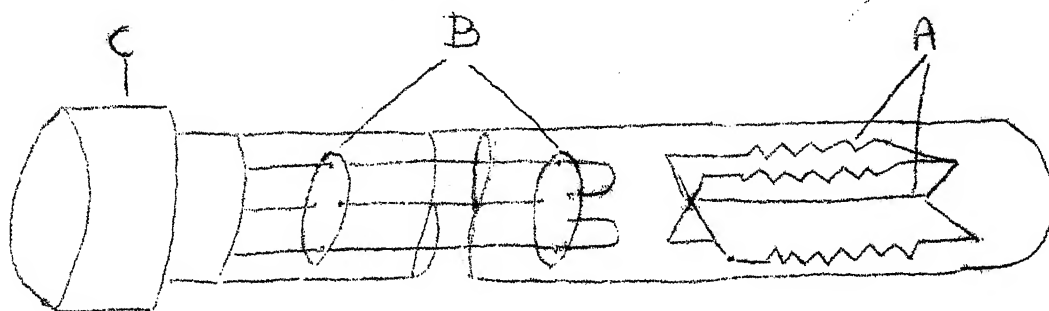
- (3) If all junctions of the circuit except one are held at constant temperature, the emf in the circuit will be a function of the temperature of the remaining junction, and can be used to measure that temperature. It is customary to prepare tables giving this emf as a function of temperature for the case where the reference junction (or junctions) are held at 0°C ." ⁶

The thermocouple is a fairly accurate and stable temperature measuring device with rapid response and low maintenance cost. The commonest thermocouples are chromel/alumel, iron/constantan, copper constantan, and platinum/platinum-rhodium. Selection of the type of thermocouple depends on the upper and lower temperature limits the type of atmosphere surrounding the measuring junction. In the present study copper/constantan thermocouple has been selected which is suitable for -200 to 500°C range and the approximate change in emf per 100°C is 4.3 mV. It may be mentioned here that copper/constantan thermocouples are subject to continuous oxidation since the metals absorb their own oxides. For this reason such a thermocouple should not be used in strongly reducing or strongly oxidizing atmospheres. In addition to self-contamination, a similar and much more rapid fall of emf will follow any exposure to metal vapors. Mechanical failure of the hot junction can occur due to over-heating or excessive heating. Copper has a positive thermoelectric power with respect to Platinum and Constantan has a negative one. Thermocouples can be made by employing the use of two dissimilar wires, but manufacturing methods have now been standardized and normally one uses these manufactured thermocouple wires. The manufacturers

follow the simple code of putting positive wire in a redsheath and the negative wire in a blue sheath. Sheaths are used to prevent any short circuiting between the two wires. Each thermocouple type has a definite emf temperature relationship and this need not be linear. Since thermodynamic studies involve accurate temperature measurement it is intended to calibrate the thermocouple against a standard Platinum Resistance Thermometer. This over-all calibration will also take into account the uncertainties in the circuit.

The uncertainties arising in the over all circuit will briefly be mentioned. Each measuring junction has its own peculiar characteristics depending on such factors as materials, methods of joining, age, and history of junction. Yet these measuring uncertainties are small and are accounted for in overall circuit calibration. Reference (or cold junction) can introduce uncertainties of $\pm 1^{\circ}\text{F}$. These can be minimized by using the same reference junction in the field as was used in the calibration. The uncertainties can be reduced by controlling the reference junction. In this study cold junction (copper-copper and constantan-copper) has been kept at ice point. In order to reduce the errors that may occur because of the presence of air bubbles in ice and also to ensure exact melting point, ice and water are used in a slurry mixture. Copper leads of gage 20, enamel coated are used to connect the cold junction of the thermocouple to the potentiometer. These wires cause no uncertainty when they are used between the reference junctions and the potentiometer. The potentiometer introduces no uncertainty that is not accounted for in the overall calibration.

It has been mentioned earlier that the calibration is to be done against a platinum resistance thermometer. Platinum is chosen as the material for use in resistance thermometers because of its stability, ductility, resistance to oxidation, availability in a highly pure state, and absence of irregularities in its temperature vs resistivity curve. The sketch of platinum resistance thermometer is shown in figure.



A : mica cross 5 cm. long and .5 cm. diameter

B : mica spacers

C : base with binding posts.

The actual thermometer with its leads is inserted in a glass tube and hermetically sealed to a base with leads. Compensation for the change of resistance of the leads with temperature is most simply effected by installing a loop of the same wire as the leads between the base and the point where the leads are welded to the platinum wire.

According to Mueller "..... the essential elements required in precise resistance thermometry (are) a resistor properly mounted and protected, a means for measuring its resistance, and a relation between resistance and temperature". The mounting

and protection has been described already. The means for measuring resistance that is employed is a resistance recorder chart which measures resistance upto three decimal places.- third place being determined by eye estimation. The recorder employs the Wheatstone principle. As for resistance - temperature relationship, Callendar's equation describing the variation in Platinum Resistance with temperature is still pertinent. The Callendar formula is as follows:

$$t' = 100 \frac{R_t - R_0}{R_{100} - R_0} + \delta \left(\frac{t'}{100} - 1 \right) \frac{t'}{100}$$

$$= \frac{1}{\alpha} \left(\frac{R_t}{R_0} - 1 \right) + \delta \left(\frac{t'}{100} - 1 \right) \frac{t'}{100}$$

An alternate form which is completely equivalent to the above expression is

$$R_t = R_0 (1 + At' + Bt'^2)$$

A and B are related directly to α and δ .

$$A = \alpha (1 + \delta/100)$$

$$B = - \alpha \delta / 10^4$$

From the Report of Calibration for Platinum Resistance Thermometer Serial No.1781311 the following are the values for the constants.

R_0 , Resistance at the ice point

$$R_0 = 25.5814$$

Fundamental coefficient of coil

$$\alpha = .003926833$$

Delta in the Callendar formula

$$\delta = 1.496176.$$

Actually the temperature t in $^{\circ}\text{C}$ at the outside of the tube protecting the platinum resistor is given by

$t = t' + M(t')$. The small value $M(t')$ is given by

$$M(t') = .045 \left(\frac{t'}{100}\right) \left(\frac{t'}{100} - 1\right) \left(\frac{t'}{419.58} - 1\right) \left(\frac{t'}{630.74} - 1\right).$$

In our study this value $M(t')$ which serves to make the International practical scale of 1968 (IPIS-68) conform more closely to the thermodynamic scale has been omitted. The omission was not intended but is due to overlooking.

With the reported values of α , δ and R_0 and neglecting $M(t')$ a table has been generated on computer to give R_t against temperature at an interval of $.005^{\circ}\text{C}$. This table is later employed in directly reading off the temperature. It is intended to calibrate the thermocouple in the range 50°C to 180°C . A device that produces uniform temperature around the hot junction is the vapour jacket. This is a silvered, evacuated double walled unit (of dimensions I.D. = 40 mm. O.D. = 70 mm and length = 90 cm). The jacket is charged with 100 cc of pure liquid. The boiling flask is heated by means of a heating mantle. By such heating the liquid is brought in equilibrium with its own vapour. Under equilibrium conditions one can observe a constant drop rate from the tip of the thermowells for platinum resistance thermometer and the thermocouple. A steady state is reached when the recorder pen moves in a vertical line and there are very little or no fluctuations. Pressure is maintained constant. At this point the R_t value of platinum resistor is directly read on the

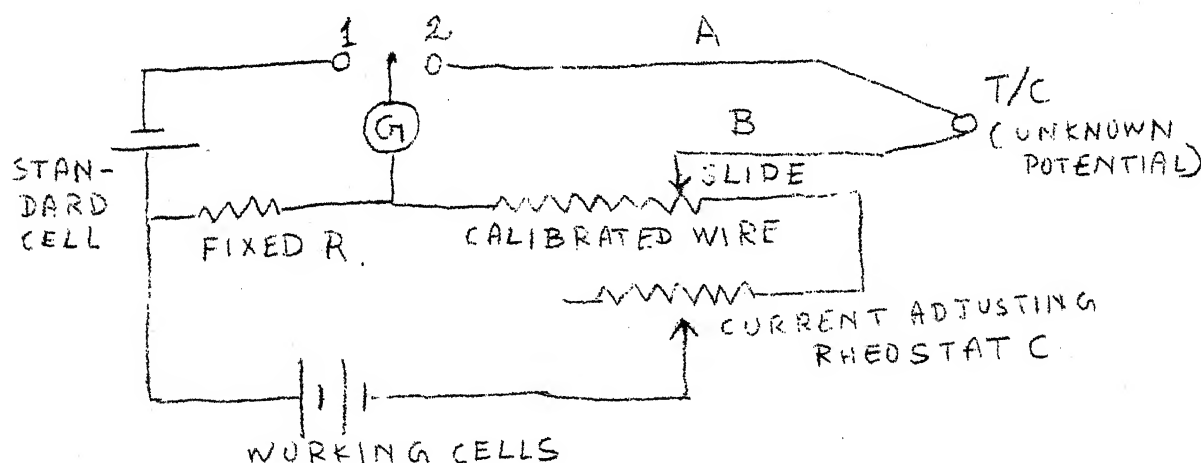
Recorder, emf in the thermocouple is read in mV from the potentiometer. To alter the temperature conditions in the vapour jacket one has to change the pressure of the system by introducing Nitrogen via the toggle valves.

Three liquids toluene, bromobenzene and naphthalene have been used in series to cover the full temperature range 50°C to 180°C. Toluene has been used for range 50 to 110°C (corresponding to 100 mm to 760 mm pressure range). Bromobenzene has been used for 110°C to 155°C (i.e. 220 mm to 760 mm) and Naphthalene for 155°C to 180°C (corresponding to 150 mm to 760 mm). Vacuum or low pressures have been maintained by plugging the vapour jacket at both ends with rubber stoppers which had been earlier soaked in kerosene to provide swelling and therefore to get a close fit. Apiezon Q was also used at both ends. Mercury was also used at the bottom to provide a seal against air bubbles etc. The top rubber stopper has holes in which the thermowells for platinum resistance thermometer and thermocouple have been inserted. The holes were made by pressing under a drill machine immediately after immersing the stopper in liquid nitrogen. Since the platinum resistance thermometer was calibrated with a 7" depth of immersion same depth has been kept under mercury in the thermowell. The thermocouple hot junction bead copper constantan has been formed by first baring the wires from their sheaths, giving them three to four twists over each other with a nose plier, dipping in borax, and showing it to the flame till the bead is seen to be formed. The oxide that may have formed is gently rubbed off with hand. Similarly

the cold junction beads (Cu/Cu and constantan/Cu) are formed. The enamel of the copper lead wire is removed by rubbing it off with sand paper.

Prior to reading off the resistance values from the recorder, the pen of the chart is brought to zero by means of the zero rheostat. The zero point is also confirmed by reading when the thermometer is at the ice point. If the R_0 value is not exactly reproduced zero rheostat is adjusted to read the required value.

Measurements of emf on the potentiometer are made after standardizing the current each time. With reference to the figure below:



The operation of the potentiometer is as follows: When the switch is placed on (1) then the current in the circuit is adjusted by means of rheostat C (Coarse and fine adjustments are possible) till there is no deflection in the galvanometer. Under this condition the current through the calibrated wire is "standardized". The switch is then placed on (2) and the slide is adjusted until the

APPENDIX 2

CALIBRATION OF REFRACTOMETER

The analysis of the vapour and liquid samples, collected after equilibrium has been reached, is done on an Abbe Refractometer with the 4th decimal place being estimated by eye. The compositions are then directly read off against the observed indices from the calibration chart. The calibration procedure is briefly described here.

Samples of known composition are prepared. The weighings are done on an electronic balance which is accurate upto the fifth decimal place. The mole fractions are calculated by the following formulae

$$x_1 = \frac{w_1/m_1}{w_1/m_1 + w_2/m_2}$$

$$x_2 = \frac{w_2/m_2}{w_1/m_1 + w_2/m_2}$$

Where w_1 and w_2 are the weights of components 1 and 2 in the sample mixture and m_1, m_2 are their respective molecular weights. About 10 to 12 samples are prepared to cover the whole range of concentration. Prior to taking any reading with the Refractometer one must secure precise adjustment of the scale in its relation to the position of the total reflecting line. This is done by reproducing the index of the glass test piece. After proper cleaning of the prisms, a small drop of bromonaphthalene (used as contact liquid) is put on the lower prism and the test piece brought in contact

with it with the engraved side up. The scale is set at the index valve engraved on the test piece. The illuminant is swung in position directly in line with the prism surface, lamp shield adjusted to secure the best contrast between the two halves of the field. The compensator dial is turned until the dividing line is correctly compensated (red at one end and blue at the other). This position of the compensator dial is then maintained for all readings.

The prism is maintained at 30°C during all the readings by circulating water from a constant temperature bath. The bath temperature is controlled by on-off heaters and the required temperature (30°C in our case) is set on a Beckman thermometer. The output of the bath is connected to the prism coupling in which the thermometer is mounted. The temperature was controlled to approximately 1°C in order to obtain consistent and accurate results. Also it was necessary to keep the temperature constant for a reasonable period of time since the prism temperature always lags behind the bath temperature.

For analysis of the samples, thorough cleaning, by an organic solvent, of the prism between samples is necessary. The liquid is introduced through a dropper and the prisms are then closed slowly squeezing out the excess. The scale is set at the approximate value expected and the borderline is brought upon the intersection of the cross hairs by means of coarse and fine hand controls. The index is then read by depressing the momentary contact switch, estimating the fourth place. All the points for

calibration were obtained in this manner. In addition the index of the pure components were also determined.

The calibration data so obtained were then regressed by applying least square technique on the polynomial $a + bx + cx^2 + \dots$ and terminating the degree of polynomial when the ratio of the variances which forms an F-distribution (experimental and control group) satisfied the 95% confidence limit.

APPENDIX 3DETAILS OF STANDARDIZATION

In this chapter it is intended to follow up the development and evaluation of the apparatus, part by part, studying each minor detail both regarding construction and operation, so that we may have a fuller appreciation of our equilibrium study.

The Equilibrium Still:

The standardization of the equilibrium still involved some major changes. With the first installation of the separation chamber and reboiler it was observed that the normal boiling point of pure carbon tetrachloride was not reproduced in the thermowell. The measured temperature, even after several hours of running and all precautions regarding insulation, was 73°C - about 5 to 6°C less than the true boiling point. Close examination revealed that there was (i) no movement of vapour and liquid slugs in the Cottrell pump and (ii) no liquid seal around the thermowell in the separation chamber with the resultant escape of vapours into the liquid-side condenser. Reduction in diameter of the Cottrell pump from 10 mm I.D. to 7 mm I.D. brought about the much needed slug formation with resultant transfer of boiling liquid from the reboiler to the separation chamber. This brought about an increase in the temperature reading, for now the liquid around the thermowell was in rapid recirculation, and no longer formed a dead pocket. However, the vapour entrainment still remained a problem and this meant that the inclination of the thermowell had to be changed

so that liquid seal may be formed. Separation chamber was constructed a second time with the thermowell now making an angle of 30° to the horizontal line instead of the initial 10° . All the dimensions of the separation chamber were also scaled down by a factor of 8. The diameter of the orifice connecting the packed chamber to the thermowell was also reduced so that the hold-up volume may reduce.

Reboiler size was reduced to an effective volume of 160cc. The stop-cock for draining material from the reboiler was eliminated completely because the grease applied to it was being eaten away by the liquid, and without grease the stop-cork was leaking even at 760 mm Hg. A seal (4" high and parallel to the Cottrell pump) was provided which could be cut at the time of draining and the material taken out through a syringe.

Under running condition of the equilibrium still the reboiler should be filled upto the neck (bottom tip of the Cottrell pump) so that the liquid may be drawn up the Cottrell pump in form of slugs. Before starting liquid level should be between 4" to 6" in the Cottrell pump. This required a total charge of 200 cc of the liquid mixture (40cc in excess of the actual volume of the reboiler). The excess charge accounted for the hold-up in separation chamber and receiver -mixer under running condition.

The performance of the Cottrell pump was measured by estimating the ratio L/V i.e. ratio of liquid to vapour recirculation rate. And the intensity of heating was measured by

estimating the vapour recirculation rate (counting the drop rate at the tip of the constriction provided in the vapour condenser), High vapour recirculation rate (proportionately controlled by voltage) gave reproducible results for the pure components. But a beyond a certain value this caused flooding of the receiver-mixer. This is the point of superheating. Flooding of the receiver-mixer should therefore be avoided at all costs.

The equilibrium points for pure components were measured under the following conditions.

	L/V (ratio of liquid to vapour recirculation rate)	V (vapor recir- culation rate)	Heat supply to external heater	Heat supply to finger heater
C_7H_{14}	3:1	200 drops/min.	20 volts	55 volts
$C_7H_{14}O$	1:1	400 drops/min.	25 volts	77 volts

When data were collected starting with pure methylcyclohexane voltage was gradually increased and when it was collected from the pure methylcyclohexanol end voltage was gradually decreased.

During the whole process of operation all the essential parts of the equilibrium still viz - separation chamber, receiver-mixer, reboiler, cottrell pump and the recycle lines are kept insulated by glass wool. Ideally the operation should be performed in adiabatic surroundings.

Single Stage Ebulliometer:

Like the equilibrium still the ebulliometer used for pressure measurement of the system has been lagged with glass wool.

About 60 cc of pure benzene are necessary for slug formation in the Cottrell pump. The liquid is both filled in and drained out from the top of the condenser. This method eliminated the use of a stop cork for draining the liquid, it was necessary because the grease in the stop cork was being eaten away by benzene. In addition to the condenser an ice trap was provided at the top to prevent any escape of benzene vapours into the manifold. The ebulliometer is plugged to the manifold with a B12 ground glass joint.

A constant boiling point of benzene is reproduced for a condensation rate of 70 to 120 drops/min. The voltage was fixed at 19 volts to get a drop count of about 100 drops/min. The resistance of the heating element was 20 ohms.

Differential Ebulliometer:

The whole differential ebulliometer has been lagged with asbestos and magnesia powder mixture and on top of it with glass wool and asbestos tape. Amount of charge required for slug formation in the Cottrell pump is equal to 60 cc. A microheater has been provided near the top drop counter to boost the flow of vapors and prevent partial condensation occurring on the walls due to heat loss.

The differential ebulliometer was standardized with respect to benzene. Both the thermowells indicated a temperature of 80.1°C at 760 mm Hg when (i) main heater was at 30 volts and the microheater was at 6 volts and (ii) the drop counts were 30 drops/min. and 100 drops/min in the top and bottom drop counter respectively.